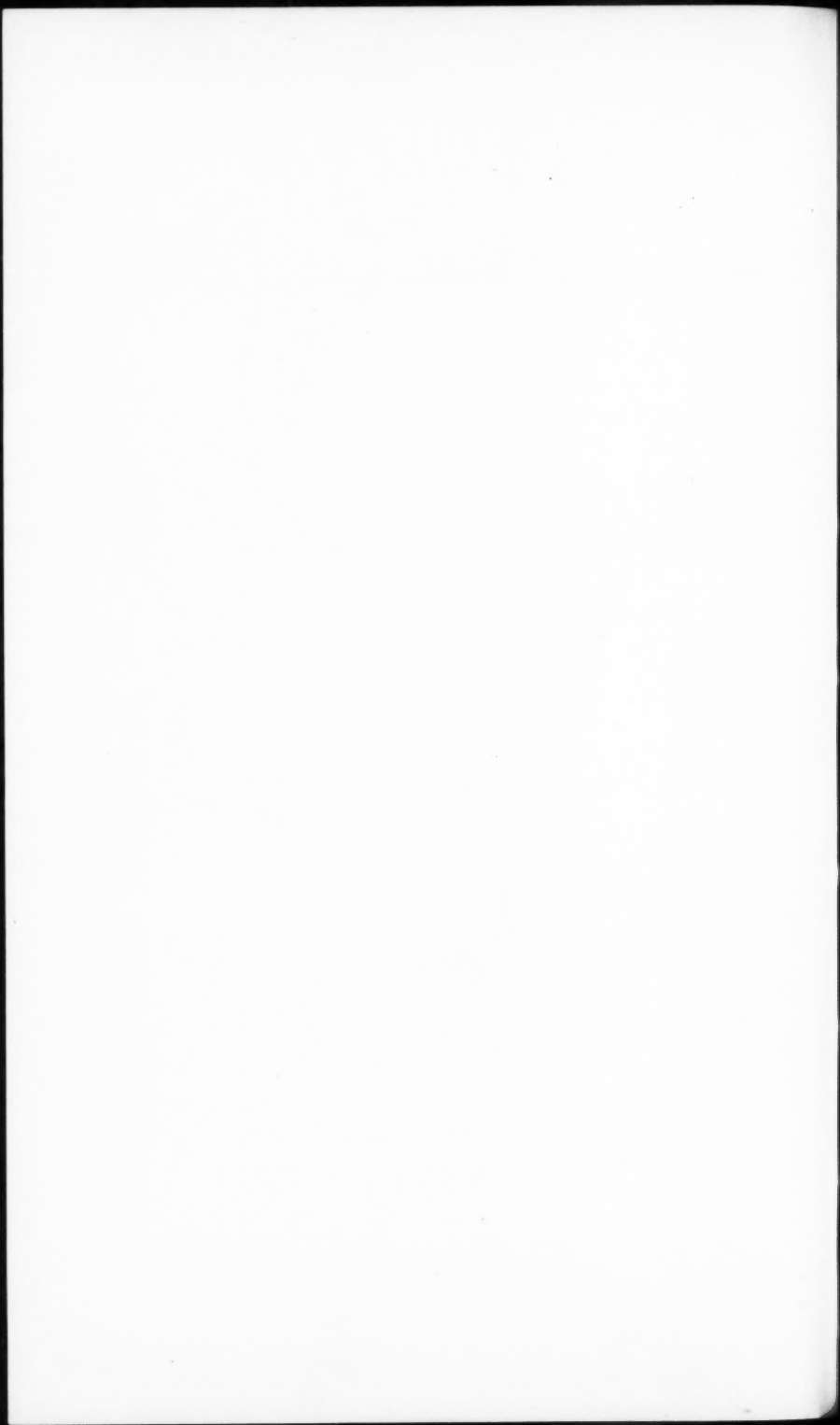


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A NEW EQUATION OF STATE FOR FLUIDS.

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1. INTRODUCTION.

The functional relationship between the pressure, volume and temperature of a fluid, commonly called the equation of state, has been the subject of many papers since the investigations of Boyle and Charles led to the formulation of the perfect gas law. It was soon recognized that this simple equation represents the behavior of actual gases to the first approximation only, as large differences between observed and calculated values occur except in the region of low pressures. Many modifications have been suggested in order to represent more accurately the relation between the measured pressures, volumes and temperatures of a gas or liquid, and of these the

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best known are the equations of state proposed by van der Waals,¹ Lorentz,² Clausius,³ and Dieterici.⁴

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \quad (\text{van der Waals})$$

$$p = \frac{RT}{V^2} [V+B] - \frac{A}{V^2} \quad (\text{Lorentz})$$

$$p = \frac{RT}{V-b} - \frac{a}{T(V+c)^2} \quad (\text{Clausius})$$

$$p = \frac{RT}{V-b} e^{-\frac{a}{VRT}} \quad (\text{Dieterici})$$

which represent second order approximations.

As more accurate experimental data became available, still further or third order modifications were introduced. To this class belongs the equation of state of Keyes⁵ which, for a non-associating gas, has the form

$$p = \frac{RT}{V - \beta e^{-\alpha/V}} - \frac{A}{(V+l)^2} \quad (\text{Keyes})$$

This equation has been extensively compared with experimental data and applied to the calculation of various thermodynamic properties of fluids.⁶ It reproduces the measured pressures very satisfactorily for specific volumes greater than about 15 cubic centimeters per gram.

Much of the pressure-volume-temperature data on gases has resulted from the investigations of Kamerlingh Onnes and his associates at the University of Leiden, and from those of Holborn, Schultze and Otto at the Physikalisch-Technischen Reichsanstalt in Berlin. Neither of these groups of workers use any of the theoretical equations of state now existent but express their results in the form of empirical expansions,

$$pV = A + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^4} + \frac{E}{V^6} + \dots \quad (\text{Leiden})$$

$$pV = a + bp + cp^2 + dp^4 + \dots \quad (\text{Berlin})$$

There is one such expression for each isotherm so that the parameters A, B, C, \dots and a, b, c, \dots are functions of the temperature. A and a can be associated with RT but each of the other parameters

require a four or five term equation in order to represent the data over the experimentally studied temperature range.

Thus it appears that the simple equations of state with a more or less theoretical background do not reproduce the experimental measurements over a wide range of pressure and temperature with sufficient accuracy for all requirements, whereas the empirical equations require a large number of terms in order to represent a comparatively large field, and consequently are not convenient for use in thermodynamic calculations.

Practically all theoretical equations of state express p as an explicit function of V and T , and may be written in the generalized form

$$p = T \psi(V) - \phi(V) - F(V, T) \quad (1)$$

In the equations of van der Waals, Lorentz and Keyes (for a non-associating gas), $F(V, T) = 0$; Clausius places $\phi(V) = 0$; while the equation proposed by Dieterici, when the exponential is expanded, contains all three of these functions.

In the present paper, the authors propose the equation of state⁷

$$p = \frac{RT(1 - \varepsilon)}{V^2} [V + B] - \frac{A}{V^2} \quad (2)$$

in which

$$A = A_0 \left(1 - \frac{a}{V} \right)$$

$$B = B_0 \left(1 - \frac{b}{V} \right)$$

$$\varepsilon = \frac{c}{VT^3}$$

This equation is of the general form of (1) and the functions $\psi(V)$, $\phi(V)$ and $F(V, T)$ can be obtained by rearrangement of (2) into the form

$$p = \frac{R}{V^2} [V + B] T - \frac{A}{V^2} - \frac{Rc}{V^3} [V + B] \frac{1}{T^2} \quad (3)$$

In the preceding equations, the gas constant R has the same value on the molal basis for all gases, and A_0 , a , B_0 , b , and c are constants whose values depend upon the kind of gas under consideration.

It is believed that this equation of state has the following desirable properties: easy and unique evaluation of the constants from the

pressure-volume-temperature data, accurate reproduction of the experimental pressures and their derivatives over the entire measured temperature range and over a wide range of densities, simplicity of mathematical form, and adaptability of the volume and temperature functions to further expansion, if necessary.

In the following sections a theoretical basis for this equation is given, a detailed method for obtaining the constants from the pressure-volume-temperature data is outlined, a study of the accuracy of evaluation of the constants is made, and a comparison is given between the observed pressures and those calculated from the equation for the ten gases helium, neon, argon, hydrogen, nitrogen, oxygen, air, carbon dioxide, methane and ether, together with a comprehensive bibliography of the compressibility data. Finally some suggestions concerning the use of the equation in thermodynamic calculations are included.

2. GENERAL EXPERIMENTAL CONDITIONS IMPOSED UPON AN EQUATION OF STATE.

In thermodynamics it is taken as axiomatic that for a given mass of any isotropic system in which mechanical work only is concerned, there exists a relation of the form $f(p, V, T) = 0$ between the variables which define the state of the system. Theory demands no unique form for this function nor does it specify which of the variables, or combinations of them, is to be regarded as dependent. However, kinetic theory has developed mainly from a consideration of pressure as the dependent variable, and the majority of equations of state are in accord with this. On the other hand, pressure and temperature are the usual properties measured and varied in experimental procedure and, from this viewpoint, are more naturally the independent variables. Unfortunately no adequate theory seems to be existent for developing volume as an explicit function of pressure and temperature, and until such theory appears, it seems necessary to express theoretical equations of state in the form $p = f(V, T)$.

The laws of thermodynamics impose no restrictions on the form of the equation of state but kinetic theory and well-established experimental evidence do so. One of these restrictions is concerned with the form which the equation assumes in the limit as the pressure (or density) is decreased at any constant temperature, while another applies to the limiting form as the temperature is increased at any constant density. In this paper, the region immediately around the

critical point is not considered and no reference will be made to the relations demanded of equations at this point. Also the possibilities of dissociation of the simple molecular species and of chemical reaction between different species in a mixture are excluded.

It appears to be well established that, as the pressure on a gas is reduced at constant temperature, the pressure-volume product approaches the ideal gas value, namely

$$\lim_{p \rightarrow 0} pV = RT$$

and this would seem to be true regardless of the temperature, excluding as mentioned above, the effect of dissociation. But it is also true that a considerable number of the thermodynamic derivatives do not reduce in the limit to the form given by the perfect gas law. For example, in the case of all actual gases

$$\lim_{p \rightarrow 0} \left(\frac{\partial pV}{\partial p} \right)_T \begin{matrix} \geq \\ \leq \end{matrix} 0 \text{ if } T \begin{matrix} \geq \\ \leq \end{matrix} T_B$$

where T_B is the Boyle temperature, whereas the limit of this derivative is zero under all conditions for a perfect gas. In this respect, a real gas becomes more imperfect as the temperature increases above the Boyle point.

A most outstanding phenomenon in connection with all real gases is the close approach to linearity of the pressure-temperature lines of constant density, the so-called isometrics. This fact has long been known,⁸ and has led some investigators⁹ to measure pressures for the same set of densities on each isotherm. At high densities, the curvature of the isometrics is very well defined, but with decreasing density, it approaches zero as a limit. On the basis of his experimental data, Young¹⁰ considered that

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_V \begin{matrix} \leq \\ \geq \end{matrix} 0 \text{ if } V \begin{matrix} \geq \\ \leq \end{matrix} V_c$$

where V_c is approximately the critical volume, and it is now definitely established that in the gaseous region, the curvature is negative.

Further, the experimental data seem to show that, at any density the curvature of the isometrics becomes less with increasing temperature, and hence,

$$\lim_{T \rightarrow \infty} \left(\frac{\partial^2 p}{\partial T^2} \right)_V = 0$$

or in other words, the isometrics approach linearity at high temperatures.¹¹

In general, equations of state can be written in the form of relation (1)

$$p = T \psi(V) - \phi(V) - F(V, T) \quad (1)$$

which can be rearranged or expanded into the form

$$pV = RT + \frac{1}{V} f_1(T) + \frac{1}{V^2} f_2(T) + \frac{1}{V^3} f_3(T) + \dots \quad (4)$$

Equation (1) is more convenient for the study of properties at constant volume, whereas (4) is more adapted for use at constant temperature. The various conditions imposed on equations of state can now be summarized by reference to (1) and (4). For all actual gases, the following relations can be written.

I. At constant temperature—from Equation (4)

(a) $\lim_{1/V \rightarrow 0} pV = RT$

(b) $f_1(T) \neq 0$, otherwise $\lim_{1/V \rightarrow 0} \left(\frac{\partial pV}{\partial p} \right)_T = 0$ for all temperatures.

II. At constant volume—from Equation (1)

(c) $\lim_{T \rightarrow \infty} F(V, T) = 0$, i. e. $\lim_{T \rightarrow \infty} \left(\frac{\partial^2 p}{\partial T^2} \right)_V = 0$ for all volumes.

(d) $\lim_{1/V \rightarrow 0} F(V, T) = 0$, i. e. $\lim_{1/V \rightarrow 0} \left(\frac{\partial^2 p}{\partial T^2} \right)_V = 0$ for all temperatures.

(e) $F(V, T) > 0$, i. e. $\left(\frac{\partial^2 p}{\partial T^2} \right)_V < 0$

Relations (a) and (b) illustrate the isothermal conditions that, for the calculation of pV , the equation of state for real gases must approach that for an ideal gas as the density is decreased, but not for the calculation of certain derivatives. Equation (e) indicates that the curvature of the isometrics of a gas is always negative, whereas (c) and (d) show that the isometrics approach linearity at high temperatures, and also with decreasing density. Hence (c) and

(e) are equivalent to the statement that with decreasing temperature, increasingly larger amounts must be added to the actual pressures to make the resulting isometrics linear.

Equation (1) can be put into the form

$$p' = p + F(V, T) = T \psi(V) - \phi(V) \quad (5)$$

where p' can be designated as the 'corrected pressure' since it varies linearly with the temperature at constant density. The right hand side of (5) is evidently the equation of the line to which the original isometric is asymptotic.

Equation (1) purports to be a generalized equation of state and is based on the considerations outlined in this section. In the following section the kinetic theory is used as the basis for suggestions regarding the specific form of the volume and temperature functions.

3. THEORETICAL BASIS FOR THE PROPOSED EQUATION OF STATE.

The kinetic theory is founded on the hypothesis that a gas consists of continually moving molecules or atoms, whose velocities are distributed according to certain laws; from which it is shown that the pressure and density of the gas are uniform throughout the interior. From the thermodynamic and experimental viewpoints, however, it is the pressure at the boundary which is of interest, and in general this will differ from that in the interior. In the case of actual gases, for given conditions of temperature and density, the pressure in the interior will depend, among other things, upon the forces which act between the molecules and upon their dimensions, and at the boundary this pressure will be modified by the field of force set up by the action of these intermolecular forces. It is customary to consider the effects of the forces in the interior and at the boundary as independent, so that the net pressure is that existent in the body of the gas diminished by an amount determined by the field at the boundary, although rigorously these two effects are perhaps not independent. Following the usual custom, the measured pressure of a gas can be written as the difference of two terms, one of which arises from the kinetic energy possessed by the gas, and the other from its potential energy,

$$p = p_{\text{kin.}} - p_{\text{coh.}}$$

where $p_{\text{kin.}}$ is the kinetic pressure and $p_{\text{coh.}}$ is the so-called cohesive pressure. These two terms will be considered separately.

(a) *Kinetic Pressure.*

A number of methods are available for the calculation of this pressure, among which may be mentioned the method of general dynamics,¹² the method of collisions,¹² the method of the mean free path,¹³ and that employing the Clausius virial.¹⁴ In the case of an ideal gas, namely one in which the molecules are infinitesimally small, perfectly elastic, and in which there are no intermolecular forces, these methods lead readily to the result that $p = \rho RT$ where ρ is the density of the gas. A simple method, due to Phillips,¹⁵ of obtaining this relation is to consider an imaginary plane in the interior of a vessel containing a perfect gas and to evaluate the time rate of transfer of momentum, I_i , across unit area of this plane. It is easily shown $I_i = \rho RT$. In the case of an actual gas, the transfer of momentum is not the same, and the theoretical deductions of Clausius,¹⁶ Lorentz,¹⁷ van der Waals,¹⁸ Boltzmann,¹⁹ Jeans,²⁰ van Laar,²¹ etc. have all shown that it is greater than for a perfect gas. On general considerations, Phillips has pointed out that the transfer of momentum is greater for any gas in which intermolecular forces exist regardless of whether these forces consist of repulsion or attraction, regardless of the law of such forces, and further independent of the size of the molecules, which may be infinitesimal.

The method which Phillips²² proposed for the evaluation of the volume function $\psi(V)$ of Equation (1) can be applied with slight modifications to the present case. Consider a thin section of the fluid between parallel planes which are in the interior of the fluid and which are a distance dx apart, where dx is the x -component of the distance travelled in the time dt by a molecule of class A (*i. e.* those possessing velocities between u and $u + du$). The kinetic pressure is equal to the total rate of transfer of momentum across unit area of one of these planes (called the reference plane) due to the passage of molecules of all classes, the arithmetic sum of the momenta of the molecules being taken regardless of the direction of passage through the plane.

Consider now the molecules of class A contained in a cylinder of unit area and length dx , the two ends of which lie in the parallel planes; their total momenta are $v_1 m u^2 dt$ where v_1 is the number of molecules of this class in unit volume. If, in the time dt , v_1 molecules of class A pass through the end of the cylinder lying in the reference plane, the contribution to the pressure would be $v_1 RT$ and when summed for all typed of molecules the result for the kinetic pressure

would be ρRT .²³ In the case that the molecules of the gas attract or repel each other (due to the existence of intermolecular forces) the passage of momentum is greater than this value. For, during the time, dt , which must be long enough for a large number of molecules to cross the reference plane so as to give an average value, a certain fraction of the molecules which have already passed through the plane will be reflected and pass through again, due to their interaction with other molecules. This reflection will occur across all boundaries of the cylinder equally in both directions and so will not affect the distribution in the cylinder. But the momentum of the reflected molecules must be included in any method for the calculation of the pressure. Hence, due to the reflection of the molecules through the reference plane (which may be any plane in the interior of the fluid) the value ρRT must be increased, in the ratio of the number of molecules which actually pass through the boundary to the number in the cylinder. If r is the average value of the "reflection" for all classes of molecules, there is obtained for the true rate of transfer of momentum (I_a) the relation

$$I_a = \rho RT (1 + r) \quad (6)$$

If the density of the gas is small so that the molecules act independently as reflectors, the fraction reflected is proportional to the density, and hence $r = \rho B$ so that Equation (6) becomes

$$I_a = p_{\text{kin.}} = \frac{RT}{V^2} [V + B] \quad (7)$$

This expression was first deduced by Lorentz²⁴ from the Clausius virial. If the density is such that this simple assumption of independent reflection is not valid, and the reflecting power per molecule is interfered with by those around it, B will not be constant but will be dependent upon the density, and the simplest form for this second order correction is a linear function of the density. Under these conditions

$$B = B_0 (1 - b\rho) \quad (8)$$

and (7) becomes

$$p_{\text{kin.}} = \frac{RT}{V^2} \left[V + B_0 \left(1 - \frac{b}{V} \right) \right] \quad (9)$$

In the treatment thus far, the assumption has been made that the time of encounter between the molecules is independent of the kinetic

energy, or in other words, of the temperature. That this is not strictly valid can be seen from general considerations. When two slowly moving molecules encounter one another, there is a tendency for them to move under the influence of each other for an appreciable length of time due to the intermolecular forces between them. This has the effect of decreasing the number of independent aggregates in the system, and hence simulates association or aggregation. At low temperatures the number of such slowly moving molecules is greater than at higher temperatures and a correction must be made for this. Clausius²⁵ attempted to account for this effect by making the cohesive pressure term vary as the reciprocal temperature. Boltzmann,²⁶ Gibbs,²⁷ and Keyes and Taylor²⁸ have all treated aggregation by a modification of the kinetic pressure term, as have also Boynton and Bramley.²⁹ The variation of the average time of encounter with the temperature has the same effect as a change in the average molecular weight of the gas and hence the gas constant R may be considered to depend upon the temperature and density, since the latter also affects the number of encounters and hence the number of molecules which can be considered as independent. In a former publication, the authors,³⁰ using a method somewhat analogous to that employed by Keyes and Taylor, modified R in the following manner:

$$R' = R \left(1 - \frac{m}{V} e^{n/T} \right)$$

where m and n are constants, R the usual perfect gas constant and R' is its analogue in the equation of state of an aggregating gas. This relation was shown to reproduce the experimental data in a satisfactory manner, but was not convenient due to the use of an exponential function of the temperature. A complete treatment of the relation of the degree of aggregation to the temperature has not been given, but in general it can be assumed that to the first approximation the variation in the number of independent aggregates due to the effect on the average time of encounter is directly proportional to the density and inversely proportional to some power of the absolute temperature, so that R' becomes

$$R' = R \left[1 - f(V, T) \right] = R \left[1 - \frac{c}{VT^n} \right] \quad (10)$$

From a study of the experimental data, it has been found that $n = 3$ gives a very satisfactory reproduction of the measurements, and

the introduction of this modification into Equation (9) leads to the complete expression for the kinetic pressure,

$$p_{\text{kin.}} = \frac{RT(1 - c/VT^3)}{V^2} [V + B_0(1 - b/V)] \quad (11)$$

(b) *Cohesive Pressure.*

It has been pointed out by Phillips³¹ that whatever may be the law of force between the molecules, the potential energy will be directly proportional to the density for a given mass of gas, provided only that the law of force is independent of the density and that the force decreases with distance with sufficient rapidity for integrals having infinite limits to converge. Under these conditions the potential energy may be written

$$E = A\rho = \frac{A}{V}$$

and differentiation with respect to the volume gives the cohesive pressure

$$p_{\text{coh.}} = - \frac{\partial E}{\partial V} = \frac{A}{V^2} \quad (12)$$

which is the usual expression obtained by van der Waals and Lorentz.

In general, the forces between electrical systems are dependent upon the dielectric constant of the medium. Therefore Phillips considers that, if the molecules can be considered as substantially rigid electrical systems, the molecular forces which give rise to the cohesive pressure are affected by the dielectric constant k of the gas, and since this varies with density it must be introduced into (12). The cohesive pressure is therefore given by the relation

$$p_{\text{coh.}} = \frac{A_0}{kV^2} \quad (13)$$

The dielectric constant of a gas is related to the density by the Lorentz equation

$$\frac{k-1}{k+2} = \frac{C}{V}$$

$$k = \frac{V+2C}{V-C}$$

Substitution of this value of k into (13) and neglecting all powers of density higher than the first in the expansion gives

$$\begin{aligned} p_{\text{coh.}} &= \frac{A_0}{V^2} \left(1 - \frac{3C}{V} + \dots \right) \\ &= \frac{A_0}{V^2} \left(1 - \frac{a}{V} \right) \end{aligned} \quad (14)$$

The preceding method used for evaluating the variation of the quantity A (of Equation 12) with the density could have been applied to B , and would have given the same form of relation as assumed in (8).

Combination of (11) and (14) gives the complete equation of state,

$$p = \frac{RT(1 - c/VT^3)}{V^2} [V + B_0(1 - b/V)] - \frac{A_0}{V^2} (1 - a/V) \quad (15)$$

which is Equation (2) written in extended form.

In the deduction of (15), general physical considerations have been presented rather than detailed computation founded on the assumption of certain laws for the distribution of velocities and for the forces acting between the molecules. The first reason for this choice is that the utility of an equation of state depends largely upon its ability to reproduce the measured pressure-volume-temperature data and to give accurate values for the thermodynamic derivatives, and hence in the evaluation of the specific form of functions used much consideration was given to the representation of the experimental measurements. In the second place, (15) differs from the Lorentz equation of state, which has been deduced in a rigorous manner from the general laws of kinetic theory, only in that the three second order constants a , b and c have been introduced.

The proposed equation rests upon the two main assumptions that the kinetic and cohesive pressures can be treated separately and that the law of force (the specific form of which does not enter into the treatment) shall be such that it will diminish rapidly with distance. Both of these assumptions are common to the treatment of a large number of kinetic theory problems.

4. THE PROPOSED EQUATION OF STATE FROM THE STAND-POINT OF THE EXPERIMENTAL RESTRICTIONS.

It remains to be seen whether or not the equation of state (15) conforms to the experimental conditions which were outlined in

Section 2. When Equation (15) is written out in full and the terms rearranged, there results for the virial form

$$pV = RT + \frac{\beta}{V} + \frac{\gamma}{V^2} + \frac{\delta}{V^3} \quad (16)$$

where

$$\beta = RTB_0 - A_0 - Rc/T^2$$

$$\gamma = -RTB_0b + A_0a - RB_0c/T^2$$

$$\delta = RB_0bc/T^2$$

For a given mass of a gas, β , γ and δ are functions of the temperature only and hence are constants at a given temperature.

I. Conditions at Constant Temperature. From a consideration of Equations (16) and (4) it can be seen that at constant temperature

$$\lim_{1/V \rightarrow 0} pV = RT$$

and that $\beta = f_1(T)$, $\gamma = f_2(T)$ and $\delta = f_3(T)$. Thus conditions (a) and (b) are fulfilled. Also by differentiation of (16) there results

$$\begin{aligned} \left(\frac{\partial pV}{\partial p} \right)_T &= V + p \left(\frac{\partial V}{\partial p} \right)_T \\ &= \frac{\beta + 2\gamma\rho + 3\delta\rho^2}{RT + 2\beta\rho + 3\gamma\rho^2 + 4\delta\rho^3} \end{aligned}$$

where $\rho = 1/V$. Hence

$$\begin{aligned} \lim_{1/V \rightarrow 0} \left(\frac{\partial pV}{\partial p} \right)_T &= \frac{\beta}{RT} \\ &= B_0 - \frac{A_0}{RT} - \frac{c}{T^3} \end{aligned}$$

so that there is only one temperature at which this derivative is zero—the Boyle temperature—since this cubic in $1/T$ has only one real root.

For a study of the equation of state at constant volume, (15) may be written in the form

$$p = T\psi(V) - \phi(V) - \frac{1}{T^2} \Gamma(V) \quad (17)$$

where

$$\psi(V) = \frac{R}{V^2}[V + B] = \frac{R}{V^2}[V + B_0(1 - b/V)]$$

$$\phi(V) = \frac{A}{V^2} = \frac{A_0}{V^2}(1 - a/V)$$

$$\Gamma(V) = \frac{c}{V}\psi(V) = \frac{cR}{V^3}[V + B_0(1 - b/V)]$$

II. Conditions at Constant Volume. By a comparison of (17) with (1), it is seen that $\frac{1}{T^2}\Gamma(V) = F(V, T)$. Hence as the temperature increases at constant volume, or as the volume decreases at constant temperature, this term approaches zero as a limit, thus fulfilling conditions (c) and (d), whereas if $c > 0$ this is also true of (e).

5. DETERMINATION OF THE VALUES OF THE CONSTANTS FROM THE EXPERIMENTAL DATA.

It is of major importance that the form of an equation of state be such that the values of the constants may be determined easily and uniquely from the experimental pressure-volume-temperature measurements. With the exception of c , each of the constants of the equation presented in this paper appears as the slope or intercept of a straight line when the data are treated in a suitable manner. In order to illustrate the method of determining the values of the constants, a detailed description for the gas oxygen is given.

The compressibility of oxygen has been studied by Holborn and Otto³² over the temperature range from 0° to 100° C. and to 100 atmospheres, by Kamerlingh Onnes³² and his associates from 0° to -117° C. and to 60 atmospheres, and by Amagat³² from 0° to 200° C. and from 100 to 3000 atmospheres. Amagat's pressure measurements do not extend into the region covered by either the Berlin or Leiden investigations, and hence his data are not considered in the present paper, but will be treated in a later publication.

The values of the constants of the proposed equation of state can be most conveniently determined from those data which list the pressure for the same set of densities at each temperature. Many investigators present the results of their measurements in the form of isothermals, and they can be converted to isometrics by a modification of a method introduced by Andrews.³³

On a given isotherm, the quantity $(pV - RT)$ is calculated for each measured density, and a linear equation passed through the points of zero density [where $(pV - RT)$ is also zero] and the highest measured density. The deviations of the measured values of $(pV - RT)$ from those calculated by the linear equation are plotted against the corresponding densities on a large scale. By use of the linear equation and the deviation plot, it is possible to obtain a series of values of pV , and hence of pressure, for a set of evenly spaced densities, the same densities being used at each temperature. In Table III are listed the smoothed data on oxygen which were obtained by this method. The pressures given in this table will be called the "observed pressures."

Throughout the present paper the units used are atmospheres for pressure, degrees Kelvin for temperature, and liters per mole for volume (or moles per liter for density). The position of the ice-point on the Kelvin scale is taken as 273.13° .

(a) *The $F(V, T)$ Function.*

From Equation (5), it can be seen that if the form of function chosen for $F(V, T)$, namely

$$F(V, T) = \frac{c\psi(V)}{VT^2}$$

is accurate from the standpoint of both temperature and volume variations, there will be one value of c , which will cause the "corrected pressure"

$$p' = p + \frac{c\psi(V)}{VT^2} = T\psi(V) - \phi(V)$$

to vary linearly with the temperature for every isometric. In order to evaluate p' it is necessary to know $\psi(V)$ which is the slope $\left(\frac{\partial p'}{\partial T}\right)_V$, and since p' is not known until the additive term $F(V, T)$ has been evaluated, several approximations are required.

A provisional value for c is first obtained from a consideration of a single isometric, which should be of sufficiently high density to depart markedly from linearity, and which should also cover as long a temperature range as possible. For oxygen the isometric 3.5 moles per liter was used. A value is assumed for c and the term $F(V, T)$ evaluated at the temperatures T_2 and T_1 from the relation

$$F(V, T) = \frac{c}{VT^2} \left[\frac{p_2 - p_1}{T_2 - T_1} \right]_V = \frac{c}{VT^2} \left(\frac{\Delta p}{\Delta T} \right)_V$$

where p_2 and p_1 are the observed pressures at the highest and lowest temperatures T_2 and T_1 on the isometric. The results are added to p_2 and p_1 , giving p'_2 and p'_1 to the first approximation. The calculation is repeated using the slope $\left(\frac{\Delta p'}{\Delta T} \right)_V$ resulting from the two values of p' just obtained, and this process continued, using the extreme temperatures only, until no further change appears in $\left(\frac{\Delta p'}{\Delta T} \right)_V$. With this slope, a set of provisional values of p' at each temperature on the isometric is computed. The slope of the best line through these data is then used in the computation of the final values of the corrected pressure, which are called p'_{obs} in Tables I and II. Since the whole term $F(V, T)$ is usually small, several approximations are in general sufficient, and the actual amount of work is not large. The complete details of this calculation for oxygen are given in Table I. It should be noted that the number of approximations used in Table I is greater than necessary. Since $F(V, T)$ increases with decreasing temperature, the slope of the (p', T) curve is always less than that of the (p, T) curve, and hence the number of operations can be materially reduced by using, in the first approximation, a slope which is smaller than that given by $\left(\frac{\Delta p}{\Delta T} \right)_V$.

When the provisional value of c , which straightened the test isometric, is found, the values of p' for all of the isometrics are computed and tested for linearity. If it is considered that all of the isometrics are satisfactorily linear the provisional value of c is accepted as the final value; if not a small adjustment is made in the value of c and the calculation repeated.

In Table II, the effect of a variation in the value of c is shown. When c is increased, the numerical magnitude of the curvature of p' with T is decreased, and if c becomes too large the curvature may even pass through zero and become positive.

Tables III and IV show the effect of the term $F(V, T)$ in the equation of state. In Table III the observed pressures of oxygen are compared with those calculated from a straight line through the extreme temperatures for each isometric. It will be noticed that the curvature is always negative and that its numerical magnitude

increases with the density of the isometric. In Table IV are given the values of the corrected pressures p' , which were computed from the observed pressures of Table III by the method given above, using the value 4.8×10^4 for c . They are compared with the values calculated from the equation of the best straight line³⁴ through each isometric.

When combining the data of Holborn and Otto with those of Kamerlingh Onnes and his associates, it was found that in the case of all gases studied, the measurements of the former gave isometrics having greater curvature than those of the latter, and thus the value of c represents in each case a compromise between the two sets of measurements.

TABLE I.
DETAILS OF THE METHOD FOR DETERMINATION OF THE VALUE OF c .

Calculation of p' from an Assumed Value for c , and Test of the Linear Variation of p' with T along an Isometric.

$$p' = p + F(V, T) = T\psi(V) - \phi(V)$$

$$F(V, T) = \frac{c\psi(V)}{VT^2}; \quad \psi(V) = \left(\frac{\partial p'}{\partial T}\right)_V$$

The value of $\left(\frac{\partial p'}{\partial T}\right)_V$ is obtained by several successive approximations.

To determine if a given value of c is satisfactory, select a test isometric

- (1) which is of sufficient density for large deviations from linearity to occur, and
- (2) which extends over as wide a temperature range as possible.

For oxygen the isometric $\rho = 3.5$ mols per liter was chosen.

Assume $c = 4.8 \times 10^4$ in units of atmospheres, liters per mole, and degrees Kelvin ($T^\circ K = t^\circ C + 273.13$).

Temp. °K	156.14	157.12	159.15	163.16	170.67	193.10	233.08	273.13	323.13
$p_{\text{obs.}}$	33.00	33.37	34.10	35.58	38.25	46.21	59.97	73.64	90.41

$$\psi_1(V) = \left(\frac{\Delta p}{\Delta T}\right)_V = \frac{90.41 - 33.00}{323.13 - 156.14} = 0.3438$$

$$F_1(V, T) = \frac{4.8 \times 10^4 \times 3.5 \times 0.3438}{T^2} = \frac{57760}{T^2}$$

$F_1(V, T)$	2.37
p'_1 (1st approx.)	35.37

$$\psi_2(V) = \left(\frac{\Delta p'_1}{\Delta T}\right)_V = 0.3329$$

$$F_2(V, T) = \frac{55930}{T^2}$$

0.55
90.96

TABLE I (continued).

Temp. °K	156.14	157.12	159.15	163.16	170.67	193.10	233.08	273.13	323.13
$F_2(V, T)$	2.29								0.54
p_2' (2nd approx.)	35.29								90.95
$\psi_2(V) = 0.3333$									
$F_2(V, T) = \frac{56000}{T^2}$									
$F_2(V, T)$	2.30	2.27	2.21	2.10	1.92	1.50	1.03	0.75	0.54
p' (final)	35.30	35.64	36.31	37.68	40.17	47.71	61.00	74.39	90.95

The best straight line through these values is

$$p' = 0.33313 T' - 16.67$$

(A)

$$\left(\frac{\partial p'}{\partial T}\right)_V = 0.33313$$

$$F(V, T) = \frac{55966}{T^2}$$

No further approximations are necessary and p' (final) becomes p' (obs.)

p' (calc. from A.)	35.34	35.67	36.35	37.68	40.19	47.66	60.98	74.32	90.97
$p'_{\text{obs.}} - p'_{\text{calc.}}$	-0.04	-0.03	-0.04	± 0.00	-0.02	0.05	0.02	0.07	-0.02

TABLE II.
DETAILS OF THE METHOD FOR DETERMINATION OF THE VALUE OF c .
SELECTION OF A PROVISIONAL VALUE OF c .

$$p'_{\text{obs.}} = p_{\text{obs.}} + F(V, T).$$

$p'_{\text{obs.}}$ is calculated by the method given in TABLE I.
 $p'_{\text{calc.}}$ is calculated from the best linear equation through the values of $p'_{\text{obs.}}$
The isometric is the same as that used in TABLE I: 3.5 moles per liter.

Temp. °K	156.14	157.12	159.15	163.16	170.67	193.10	233.08	273.13	323.13
$p_{\text{obs.}}$	33.00	33.37	34.10	35.58	38.25	46.21	59.97	73.64	90.41
Assume $c = 4.0 \times 10^4$									
$F(V, T)$	1.92	1.90	1.85	1.76	1.61	1.26	0.86	0.63	0.45
$p'_{\text{obs.}}$	34.92	35.27	35.95	37.34	39.86	47.47	60.83	74.27	90.86
$p' = 0.33499 T - 17.31$									
$p'_{\text{calc.}}$	35.00	35.32	36.00	37.35	39.86	47.38	60.77	74.19	90.94
$p'_{\text{obs.}} - p'_{\text{calc.}}$	-0.08	-0.05	-0.05	-0.01	0.00	0.09	0.06	0.08	-0.08
Assume $c = 4.8 \times 10^4$									
$F(V, T)$	2.30	2.27	2.21	2.10	1.92	1.50	1.03	0.75	0.54
$p'_{\text{obs.}}$	35.30	35.64	36.31	37.68	40.17	47.71	61.00	74.39	90.95
$p' = 0.33313 T - 16.67$									
$p'_{\text{calc.}}$	35.34	35.67	36.35	37.68	40.19	47.66	60.98	74.32	90.97
$p'_{\text{obs.}} - p'_{\text{calc.}}$	-0.04	-0.03	-0.04	0.00	-0.02	0.05	0.02	0.07	-0.02

TABLE II (continued).

Temp. °K	155.14	157.12	159.15	163.16	170.67	193.10	233.08	273.15	323.13
	Assume $c = 5.6 \times 10^4$								
$F(V, T)$	2.67	2.63	2.57	2.44	2.23	1.74	1.20	0.87	0.62
$p'_{\text{obs.}}$	35.67	36.00	36.67	38.02	40.48	47.95	61.17	74.51	91.03
	$p' = 0.33152 T - 16.08$								
$p'_{\text{calc.}}$	35.68	36.01	36.68	38.01	40.50	47.94	61.19	74.47	91.04
$p'_{\text{obs.}} - p'_{\text{calc.}}$	-0.01	-0.01	-0.01	0.01	-0.02	0.01	-0.02	0.04	-0.01

For this isometric 5.6×10^4 is the best value for c . When the other isometrics were considered it was found that this was too high and hence 4.8×10^4 was chosen as the final value for c .

TABLE III.
CURVATURE OF THE ISOMETRICS OF GASEOUS OXYGEN.

Comparison of the Observed Pressures with those Calculated on the Assumption of Linear Isometrics. For each isometric the first line gives the linear equation passed through the extreme temperatures, the second line gives the observed pressure, the third the pressure calculated from the equation, and the fourth the observed minus the calculated pressure.

Temp. °C.	-116.99	-116.01	-113.98	-109.97	-102.46	-80.03	-40.05	0	0	20	50	100
Observer	L	L	L	L	L	L	L	L	B	L	B	B
Density												
moles/liter												
	Pressures in atmospheres											
0.5	$p = 0.04212 T - 0.43$											
	6.15	6.19	6.28	6.45	6.77	7.71	9.40	11.09	11.09	11.93	13.19	15.29
	6.15	6.19	6.27	6.44	6.76	7.70	9.39	11.07	11.07	11.92	13.18	15.29
	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.00

TABLE III (continued).

Temp. °C.	-116.99	-116.01	-113.98	-109.97	-102.46	-80.03	-40.05	0	20	50	100
Observer	L	L	L	L	L	L	L	L	L	B	B
Density											
moles/liter											
Pressures in atmospheres											
$p = 0.08641 T - 1.70$											
1.0	11.79	11.87	12.06	12.41	13.07	15.01	18.48	21.95	23.67	26.26	30.54
	11.79	11.88	12.05	12.40	13.05	14.99	18.44	21.90	23.63	26.22	30.54
	0.00	-0.01	0.01	0.01	0.02	0.02	0.04	0.05	0.04	0.04	0.00
$p = 0.13296 T - 3.83$											
1.5	16.93	17.05	17.35	17.90	18.93	21.92	27.27	32.61	35.25	39.22	45.78
	16.93	17.06	17.33	17.86	18.86	21.84	27.16	32.49	35.14	39.13	45.78
	0.00	-0.01	0.02	0.04	0.07	0.08	0.11	0.12	0.11	0.09	0.00
$p = 0.18171 T - 6.77$											
2.0	21.60	21.77	22.17	22.94	24.35	28.47	35.79	43.09	46.68	52.10	61.03
	21.60	21.78	22.15	22.88	24.24	28.32	35.58	42.86	46.49	51.95	61.03
	0.00	-0.01	0.02	0.06	0.11	0.15	0.21	0.23	0.19	0.15	0.00
$p = 0.23273 T - 10.53$											
2.5	25.81	26.04	26.55	27.54	29.36	34.69	44.06	53.39	57.97	64.91	76.31
	25.81	26.04	26.51	27.44	29.19	34.41	43.71	53.04	57.69	64.67	76.31
	0.00	0.00	0.04	0.10	0.17	0.28	0.35	0.35	0.28	0.24	0.00
$p = 0.28591 T - 15.04$											
3.0	29.60	29.89	30.51	31.74	33.98	40.60	52.10	63.59	77.67	91.64	
	29.60	29.88	30.46	31.61	33.76	40.17	51.60	63.05	77.35	91.64	
	0.00	0.01	0.05	0.13	0.22	0.43	0.50	0.54	0.32	0.00	

TABLE III (continued).

Temp. °C. Observer Density moles/liter	-116.99 L	-116.01 L	-113.98 L	-109.97 L	-102.46 L	-80.03 L	-40.05 L	0 L	0 B	20 L	50 B	100 B
Pressures in atmospheres												
3.5	$p = 0.34379 T - 20.68$											
	33.00	33.37	34.10	35.58	38.25	46.21	59.97		73.64		90.41	
	33.00	33.34	34.03	35.41	37.99	45.71	59.45		73.22		90.41	
	0.00	0.03	0.07	0.17	0.26	0.50	0.52		0.42		0.00	
4.0	$p = 0.40188 T - 26.72$											
	36.03	36.49	37.33	39.07	42.21	51.54			83.58		103.14	
	36.03	36.42	37.24	38.85	41.87	50.88			83.05		103.14	
	0.00	0.07	0.09	0.22	0.34	0.66			0.53		0.00	
4.5	$p = 0.46765 T - 34.30$											
	38.72	39.25	40.21	42.23	45.86	56.60			93.43			
	38.72	39.18	40.13	42.00	45.51	56.00			93.43			
	0.00	0.07	0.08	0.23	0.35	0.60			0.00			
5.0	$p = 0.53081 T - 41.80$											
	41.08	41.67	42.76	45.07	49.22	61.42			103.18			
	41.08	41.60	42.68	44.81	48.79	60.70			103.18			
	0.00	0.07	0.08	0.26	0.43	0.72			0.00			

$$T = t^{\circ}C + 273.13$$

L = Leiden data.

B = Berlin data (Holborn and Otto)

TABLE IV.
THE CORRECTED PRESSURES, p' , OF GASEOUS OXYGEN.

Comparison of the Observed Corrected Pressures along an Isometric with those calculated from a Linear Equation.

For each isometric the first line gives the best linear equation through the data, the second line gives the observed corrected pressures, the third the values calculated from the equation, and the fourth the observed minus the calculated values.

		$p'_{\text{obs.}} = p_{\text{obs.}} + \frac{4.8 \times 10^4}{VT^2} \left(\frac{\partial p'}{\partial T} \right)_V$									
Temp. °C.		L		L		L		L		L	
Observer	Density	L		L		L		L		L	
moles/liter											
0.5		6.19		6.23		6.32		6.49		6.80	
		6.19		6.24		6.32		6.49		7.75	
		0.00		-0.01		0.00		0.00		-0.01	
Pressures in atmospheres											
$p' = 0.04198 T - 0.36$											
1.0		11.96		12.04		12.22		12.56		13.21	
		11.96		12.04		12.22		12.56		15.13	
		0.00		0.00		0.00		0.00		-0.01	
$p' = 0.08581 T - 1.44$											
1.5		17.32		17.43		17.72		18.26		19.26	
		17.32		17.45		17.72		18.25		22.19	
		0.00		-0.02		0.00		0.01		-0.02	
$p' = 0.13157 T - 3.22$											
1.5		32.74		35.36		39.31		45.85		45.87	
		32.74		35.35		39.29		45.87		45.87	
		0.02		0.01		0.02		0.01		-0.02	

TABLE IV (continued).

Temp. °C. Observer Density moles/liter	-116.99 L	-116.01 L	-113.98 L	-109.97 L	-102.46 L	-80.03 L	-40.05 L	0 L	0 B	20 L	50 B	100 B
Pressures in atmospheres												
$p' = 0.17919 T - 5.66$												
2.0	22.31	22.47	22.85	23.59	24.94	28.93	36.11	43.32	43.32	46.88	52.26	61.15
	22.32	22.49	22.86	23.58	24.92	28.94	36.11	43.28	43.28	46.87	52.24	61.20
	-0.01	-0.02	-0.01	0.01	0.02	-0.01	0.00	0.04	0.04	0.01	0.02	-0.05
$p' = 0.22863 T - 8.73$												
2.5	26.94	27.15	27.63	28.57	30.30	35.43	44.57	53.76	53.79	58.29	65.17	76.51
	26.97	27.19	27.66	28.57	30.29	35.42	44.56	53.72	53.72	58.29	65.15	76.58
	-0.03	-0.04	-0.03	0.00	0.01	0.01	0.01	0.04	0.07	0.00	0.02	-0.07
$p' = 0.27987 T - 12.41$												
3.0	31.25	31.52	32.10	33.25	35.36	41.68	52.84	64.13	64.13	78.06	91.93	
	31.29	31.56	32.13	33.25	35.36	41.63	52.82	64.03	64.03	78.02	92.02	
	-0.04	-0.04	-0.03	0.00	0.00	0.05	0.02	0.10	0.10	0.04	-0.09	
$p' = 0.33313 T - 16.67$												
3.5	35.30	35.64	36.31	37.68	40.17	47.71	61.00	74.39	74.39	90.95		
	35.34	35.67	36.35	37.68	40.19	47.66	60.98	74.32	74.32	90.97		
	-0.04	-0.03	-0.04	0.00	-0.02	0.05	0.02	0.07	0.07	-0.02		
$p' = 0.38784 T - 21.42$												
4.0	39.08	39.51	40.27	41.87	44.77	53.54		84.58	84.58	103.85		
	39.14	39.52	40.30	41.86	44.77	53.47		84.51	84.51	103.90		
	-0.06	-0.01	-0.03	0.01	0.00	0.07		0.07	0.07	-0.05		

TABLE IV (continued).

Temp. °C.	-116.99	-116.01	-113.98	-109.97	-102.46	-80.03	-40.05	0	20	50	100
Observer	L	L	L	L	L	L	L	L	B	B	B
Density											
moles/liter											
4.5	42.66	43.14	44.00	45.84	49.16	59.18		94.72			
	42.69	43.13	44.03	45.82	49.16	59.13		94.73			
	-0.03	0.01	-0.03	0.02	0.00	0.05		-0.01			
5.0	46.03	46.56	47.52	49.60	53.36	64.66		104.80			
	46.04	46.53	47.55	49.57	53.34	64.62		104.87			
	-0.01	0.03	-0.03	0.03	0.02	0.04		-0.07			

Pressures in atmospheres

 $p' = 0.44482 T - 26.76$ $p' = 0.50286 T - 32.48$ $T = t^{\circ}\text{C} + 273.13$

(b) *The $\psi(V)$ and $\phi(V)$ Functions.*

It can be seen by Equation (5)

$$p' = T\psi(V) - \phi(V)$$

that for each isometric, the quantities $\psi(V)$ and $\phi(V)$ are the slope and the intercept on the p' axis of the (p', T) line. The linear equations expressing the relations between the corrected pressures and the temperatures for the isometrics of oxygen are given in Table IV, and the slopes and intercepts of these lines are the "observed values" of $\psi(V)$ and $\phi(V)$ given in Tables V and VI.

Since

$$\psi(V) = \frac{R}{V^2}[V + B], \quad \text{where } B = B_0\left(1 - \frac{b}{V}\right);$$

then

$$B = \frac{V^2 \psi(V)}{R} - V$$

and from R , V and the observed value of $\psi(V)$, a value of B can be calculated for each isometric. The quantities B_0 and B_0b are the intercept on the B axis and the slope respectively of a straight line through a graph of the calculated values of B against $\frac{1}{V}$.

Also

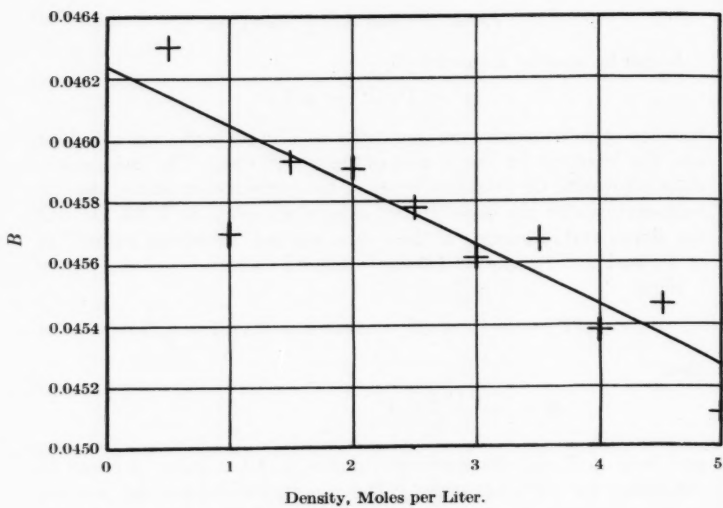
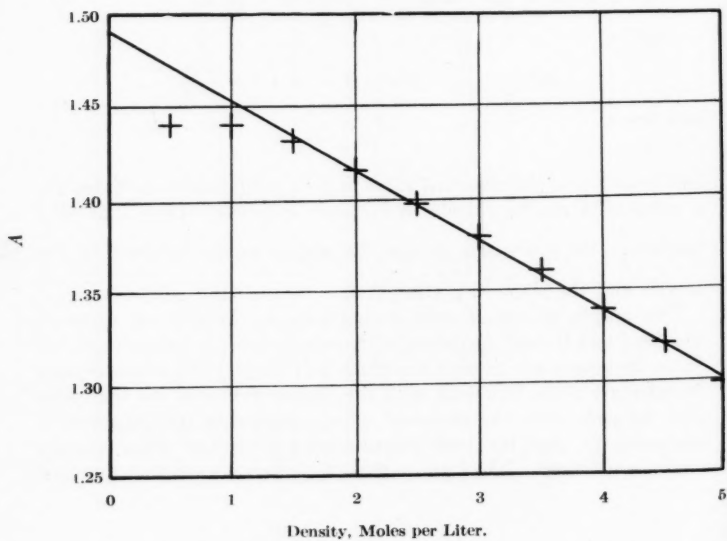
$$\phi(V) = \frac{A}{V^2}, \quad \text{where } A = A_0\left(1 - \frac{a}{V}\right)$$

and hence

$$A = V^2 \phi(V)$$

and from V and the observed value of $\phi(V)$ obtained from Table IV, a value of A can be calculated for each isometric. On a plot of A against $\frac{1}{V}$, the quantities A_0 and A_0a appear as the intercept on the A axis and the slope of a straight line through the points.

The graphs of the B and A functions for oxygen are given in Figures I and II, and the details of the calculations, in Tables V and VI. Since the graphs are indirect as regards $\psi(V)$ and $\phi(V)$, it is necessary to calculate these functions with the chosen values of the constants and compare with the observed values, adjusting the constants if necessary to give the best representation over the entire density region considered. The form of these functions is such that the most

FIGURE 1. The B Plot.FIGURE 2. The A Plot.

weight should be placed on the points in the region of high density when drawing the straight lines on the B and A plots. However, as the density of an isometric increases, the temperature range usually becomes less, and the accuracy of obtaining the functions $\psi(V)$ and $\phi(V)$ from the experimental data decreases. The experimental data on oxygen extends to a density of 9 moles per liter, but above 5 moles per liter the temperature range is only about 15° C. Hence for the determination of the values of the constants only the region below a density of 5 was used, the comparison of the observed and calculated pressures being given however over the entire density range.

The constants of the equation of state of oxygen are given in Table IX, and the comparison of the calculated with the observed pressures in Tables XV and XX. The average deviation over the whole field is 0.05 atmospheres or 0.12%, the maximum density considered being 9 moles per liter.

TABLE V.

THE $\psi(V)$ FUNCTION

$$\psi(V) = \frac{R}{V^2}[V + B]; \quad B = B_0 \left(1 - \frac{b}{V}\right)$$

$$\psi(V)_{\text{obs.}} = \left(\frac{\partial p'}{\partial T}\right)_V \text{ (from Table IV); } B_{\text{obs.}} = \frac{V^2\psi(V)_{\text{obs.}}}{R} - V$$

Density moles/liter	B		$\psi(V)$		Obs.-Calc. x 10 ⁵
	Observed	Calculated	Observed	Calculated	
0.5	0.0463	0.046143	0.04198	0.04198	0
1.0	.0457	.046045	.08581	.08584	-3
1.5	.04593	.045948	.13157	.13157	0
2.0	.04591	.045851	.17919	.17917	2
2.5	.04578	.045754	.22863	.22862	1
3.0	.04562	.045656	.27987	.27990	-3
3.5	.04568	.045559	.33313	.33301	12
4.0	.04539	.045462	.38784	.38793	-9
4.5	.04547	.045364	.44482	.44465	17
5.0	.04512	.045267	.50286	.50317	-31

$$B_{\text{calc.}} = 0.04624 \left(1 - \frac{0.004208}{V}\right)$$

$$\psi(V)_{\text{calc.}} = \frac{0.08206}{V^2}[V + B_{\text{calc.}}]$$

TABLE VI

THE $\phi(V)$ FUNCTION

$$\phi(V) = \frac{A}{V^2}; \quad A = A_0 \left(1 - \frac{a}{V}\right)$$

$$\phi(V)_{\text{obs.}} = -p' \text{ at } 0^\circ\text{K (from Table IV); } A_{\text{obs.}} = V^2\phi(V)_{\text{obs.}}$$

Density moles/liter	A		$\phi(V)$		
	Observed	Calculated	Observed	Calculated	Obs.-Calc.
0.5	1.44	1.4720	0.36	0.37	-0.01
1.0	1.44	1.4529	1.44	1.45	-0.01
1.5	1.431	1.4338	3.22	3.23	-0.01
2.0	1.415	1.4147	5.66	5.66	± 0.00
2.5	1.397	1.3956	8.73	8.72	+0.01
3.0	1.379	1.3765	12.41	12.39	+0.02
3.5	1.361	1.3574	16.67	16.63	+0.04
4.0	1.339	1.3383	21.42	21.41	+0.01
4.5	1.321	1.3192	26.76	26.71	+0.05
5.0	1.299	1.3001	32.48	32.50	-0.02

$$A_{\text{calc.}} = 1.4911 \left(1 - \frac{0.02562}{V}\right)$$

$$\phi(V)_{\text{calc.}} = \frac{A_{\text{calc.}}}{V^2}$$

6. THE EFFECT OF SMALL VARIATIONS IN THE VALUES OF THE CONSTANTS.

It is perhaps of interest to discuss the allowable variation in the values of the constants of the equation of state in order that the pressure may be calculated to any desired accuracy. Consider the equation in the form

$$p = T\psi(V) - \phi(V) - F(V, T)$$

Now since

$$T\psi(V) = \frac{RT}{V^2} [V + B], \quad B = B_0 \left(1 - \frac{b}{V}\right)$$

the error $\Delta[T\psi(V)]$ and fractional error $\frac{\Delta[T\psi(V)]}{T\psi(V)}$ produced by the variations δB_0 , δb , and δR are given by the following equations:

$$(a) \quad \Delta[T\psi(V)] = \frac{RT}{V^2} \left(1 - \frac{b}{V}\right) \delta B_0 = \frac{RTB}{V^2 B_0} \delta B_0$$

$$\frac{\Delta[T\psi(V)]}{T\psi(V)} = \frac{B}{V + B} \frac{\delta B_0}{B_0}$$

$$(b) \quad \Delta[T\psi(V)] = -\frac{RT}{V^3} B_0 \delta b$$

$$\frac{\Delta[T\psi(V)]}{T\psi(V)} = -\frac{bB_0}{V(V+B)} \frac{\delta b}{b}$$

$$(c) \quad \Delta[T\psi(V)] = \frac{T\psi(V)}{R} \delta R$$

$$\frac{\Delta[T\psi(V)]}{T\psi(V)} = \frac{\delta R}{R}$$

and since

$$\phi(V) = \frac{A}{V^2}, \quad A = A_0 \left(1 - \frac{a}{V}\right)$$

the error and fractional error in $\phi(V)$ produced by the variations δA_0 and δa are

$$(d) \quad \Delta\phi(V) = \frac{\phi(V)}{A_0} \delta A_0$$

$$\frac{\Delta\phi(V)}{\phi(V)} = \frac{\delta A_0}{A_0}$$

$$(e) \quad \Delta\phi(V) = -\frac{A_0}{V^3} \delta a$$

$$\frac{\Delta\phi(V)}{\phi(V)} = -\frac{A_0 a}{V A} \frac{\delta a}{a}$$

Also

$$F(V, T) = \frac{c\psi(V)}{VT^2}$$

and the effect of a variation δc is given by the equations

$$(f) \quad \Delta F(V, T) = \frac{F(V, T)}{c} \delta c$$

$$\frac{\Delta F(V, T)}{F(V, T)} = \frac{\delta c}{c}$$

In Table VII are given the allowable variations and fractional variations in the several constants which will each cause an error of 0.1% in the calculation of the pressure of oxygen at the densities 1

TABLE VII.
ALLOWABLE VARIATIONS IN THE CONSTANTS OF THE EQUATION OF STATE WHICH WILL EACH CAUSE A VARIATION OF
0.1% IN THE CALCULATED PRESSURE OF OXYGEN.

These values divided by 6 give the allowable variations which would together produce a total error of 0.1% in the calculated pressure.

Symbol	$\rho = 1 \text{ mole/liter}$			$\rho = 6 \text{ moles/liter}$		
	Value	Absolute error	% Error	Value	Absolute error	% Error
R	0.08206	0.000079	0.097%	0.08206	0.000066	0.081%
A_0	1.4911	0.0318	2.13	1.4911	0.0061	0.41
a	0.02562	0.02079	81.1	0.02562	0.00058	2.27
B_0	0.04624	0.00102	2.20	0.04624	0.00018	0.38
b	0.004208	0.02192	521.	0.004208	0.00061	14.6
c	4.8×10^4	4.96×10^4	103.	4.8×10^4	0.69×10^4	14.5
B	0.046045			0.045073		
$\psi(V)$	0.085838			0.625513		
$T\psi(V)$	32.029			233.398		
A	1.4529			1.26189		
$\phi(V)$	1.453			45.428		
$F(V, T)$	0.030			1.294		
P	30.546	0.031	0.10	186.676	0.187	0.10

TABLE VIII.

ALLOWABLE VARIATIONS IN THE CONSTANTS OF THE EQUATION OF STATE WHICH WILL EACH CAUSE A VARIATION OF 0.1% IN THE CALCULATED PRESSURE OF OXYGEN.

Symbol	$t = -100^{\circ}\text{C.}$			$\rho = 6 \text{ moles/liter}$		
	$\rho = 1 \text{ mole/liter}$					
	Value	Absolute error	% Error	Value	Absolute error	% Error
R	0.08206	0.000072	0.088%	0.08206	0.000046	0.056%
A_0	1.4911	0.0133	0.89	1.4911	0.0019	0.13
a	0.02562	0.00872	34.0	0.02562	0.00018	0.69
B_0	0.04624	0.00093	2.01	0.04624	0.00012	0.26
b	0.004208	0.01997	475.	0.004208	0.00043	10.
c	4.8×10^4	0.46×10^4	9.5	4.8×10^4	0.046×10^4	0.95
B	0.046045			0.045073		
$\phi(V)$	0.085838			0.625513		
$T\phi(V)$	14.861			108.295		
A	1.4529			1.2619		
$\phi(V)$	1.453			45.428		
$F(V,T)$	0.137			6.010		
P	13.271	0.013	0.10	56.857	0.057	0.10

mole per liter and 6 moles per liter and at 100° C; and in Table VIII the same information is given for -100° C. As the density increases or as the temperature decreases, the allowable variations in the values of the constants become smaller. Thus as mentioned in the preceding section when determining the constants from the experimental data, most attention is given to the high density data when drawing the straight lines on the *B* and *A* plots; and the value of *c* depends largely on the low temperature high density measurements where the function *F* (*V*, *T*) is large.

7. DISCUSSION OF THE EXPERIMENTAL DATA.

The references to all of the data considered in this paper are listed in the Bibliography, which gives the temperatures in degrees centigrade (unless otherwise noted) of the isotherms studied by each investigator as well as the pressure range in atmospheres over which the measurements extended.

General Considerations. For all gases for which comparison is possible—helium, neon, argon, hydrogen, nitrogen, oxygen, and air—the data of Holborn and Otto, when converted into constant volume form, gave isometrics with greater curvature than those of Kamerlingh Onnes and his collaborators; in fact, at higher temperatures, above 100° C., the curvatures of the isometrics of Holborn and Otto for some gases increased with temperature. Hence in obtaining a value for the equation of state constant *c*, which depends directly upon the curvature of the isometrics, the mean between the curvatures of the two sets of data was used.

Holborn and Otto, and Holborn and Schultze in general made measurements at about 25, 50, 75, and 100 atmospheres on each isotherm. The temperatures varied several hundredths of a degree, and were reduced by the experimentators to even values. Besides presenting the original data, they also gave an equation for each isotherm expressing *pV* in the form of a power series in *p* as well as smoothed tables listing, for each temperature, the *pV* product for even intervals of pressure. Pressures were expressed in terms of meters of mercury and the unit of *pV* was the value at 0° C. and one meter of mercury.

Kamerlingh Onnes and his collaborators measured at unevenly spaced temperature intervals, and sometimes several isotherms for the same gas differed by only a few hundredths or tenths of a degree. In other cases low pressure data were given for one temperature, and

higher pressure measurements at a closely nearby temperature. For some isotherms, equations were given expressing pV as a function of the density. The unit of pressure was the atmosphere, and pV was expressed in terms of the value at 0° C. and one atmosphere.

Penning (Leiden Comm. 166) has pointed out that the earlier data obtained at Leiden with the "divided piezometer" contains an unknown volume error due to the soldered connection between the glass and the steel capillaries, which connect the two parts of the piezometer. This error may be small and probably does not effect the results until the density of the gas becomes large.

Two isotherms which differed by only a few hundredths of a degree were reduced to the temperature of one of them or to an intermediate temperature. When smoothing the data to even densities as described in Section 5, the appropriate values of T were used in evaluating for each isotherm the quantities $(pV - RT)$, which were then treated as though they were derived from the same isotherm. The appropriate value of T was also used in the calculation of pV at the even densities from the smoothed differences $(pV - RT)$. The temperature scales of the various experimenters differed somewhat, and the values of T used for the calculations presented in this paper were obtained in all cases by adding 273.13 to the centigrade temperatures listed by the observers.

The data of Amagat were not used except for gaseous carbon dioxide. For no other gas considered in the present paper did he give accurate measurements below 100 atmospheres, and since practically all of the data of Leiden and the Reichsanstalt were below this pressure, there was not sufficient overlapping for a good correlation.

For the seven gases mentioned above, the equations of state rest on a combination of the data of Holborn and Otto and Kamerlingh Onnes and his co-workers, about equal weight having been given to both sets of measurements. In some cases—hydrogen, nitrogen, and air—the equations so obtained were used to calculate values for comparison with the data of other observers.

In general, when an equation was passed through the data of either of the above two sets of measurements alone, the deviations for this group between observed and calculated pressures were about one-half of the deviations obtained by using an equation based on both groups. This would seem to indicate that the consistency of a set of data taken by one observer is usually greater than the absolute accuracy of the

data. It is believed that by combining all the latest data, the best average values for the constants were obtained.

Helium, Neon, and Argon. Only the measurements made at Leiden and the Reichsanstalt were used. In averaging the deviations for helium, the isotherms below -252°C. were omitted, as the pressures were so low that a disproportionately large percentage deviation resulted. The deviations in atmospheres were about the same magnitude as those for the rest of the field.

Hydrogen. The equation is based on the Leiden and Reichsanstalt measurements. The temperatures of the Onnes and Braak isotherms were reduced to the Kelvin scale by Penning (Leiden Comm. 165(b)). The low temperature data of Crommelin and Swallow could not be correlated with the rest of the field as their isometrics had positive curvature.

The lowest pressure measured by Bartlett (at 0°C.) and by Verschoyle (at 0° and 20°) was about 50 atmospheres. The data of these observers on hydrogen were not used in the present paper but will be considered in a later publication covering the high pressure range.

There is quite an extensive set of measurements by Witkowski, and the equation derived from the Leiden and Reichsanstalt data was used to calculate values for comparison with his measurements. The agreement was good and his deviations are averaged with the others, although most of his points show positive deviations from the equation.

Nitrogen. The equation based on the Leiden and Reichsanstalt measurements agreed quite well with the 0°C. isotherm of Bartlett, and the 0° and 20° isotherms of Verschoyle. This is the accepted equation for nitrogen.

The data of Smith and Taylor could not be correlated with the measurements of the other investigators. A special equation was passed through the Smith and Taylor data, and it showed that their measurements are very consistent, except for the region below a density of 5 moles per liter, which depends on a single isometric.

Oxygen. The data of Holborn and Otto and of Kuijpers are in good agreement. The measurements of Nijhoff and Keesom covered such a short pressure range that they were not considered.

Air. The measurements of Holborn and Schultze, Witkowski, Koch and Penning were all used in the determination of the constants. The -130° to -145° isotherms of Witkowski were omitted due to the impossibility of correlating them with the rest of the field.

Carbon Dioxide. Only the 0 to 100 atmosphere data of Amagat were used for determining the values of the constants.

The measurements of Andrews, which were expressed relative to air, were transformed to absolute values using the Reichsanstalt data on air. The temperatures of Andrews' isotherms varied several tenths of a degree from point to point and each reading was corrected to a mean value of the temperature. The 21.5° isotherm had only one point in the gas region, and the 100°, 63.75°, and 48.1° isotherms show extreme variations from Amagat's data and hence are omitted from the average. The equation based on Amagat's values was used in calculating Andrews' data.

Methane. The measurements of Keyes and Burks supersede those of Keyes, Smith and Joubert and the equation is derived for the former data alone. Amagat's older measurements were not considered.

Ether. The data of Beattie alone were used. The original measured pressures, and not the smoothed values, are given. The densities were converted from grams per c.c. to moles per liter, otherwise no change was introduced.

8. DISCUSSION OF THE COMPARISON OF THE EQUATION WITH THE MEASUREMENTS.

In Table IX are given the values of the constants for the ten gases obtained by the method outlined in Section 5. The data used for the determination of the constants are critically examined in Section 7.

The comparisons of the observed pressures (smoothed to even values of the density but not smoothed for temperature) with those calculated from the equation of state are given in Tables X to XIX and a summary of the average deviations and average percentage deviations is given in Table XX.

In the tables for each gas, the observed pressures and the observed minus the calculated pressures are listed. The average deviation in atmospheres and percent are given for each isometric and for the whole field considered. With very few exceptions, all of which are mentioned as footnotes to the tables or in Section 7, all of the recent data, which cover any considerable temperature and density range, were considered and included in the averages.

The entire experimental temperature range was included in the comparison for all gases except Amagat's data above 100° C. on carbon dioxide. For several of the gases the entire measured density range was not used. In some instances the data in the region of

higher density were fragmentary, in other cases the temperature range was small. In the Bibliography are given the complete range of pressures measured on each isotherm and comparison with the tables will show what densities are omitted in the latter.

Comparisons of observed and calculated pressures for the ten gases were made at 1777 points and the general average deviation was 0.08 atmospheres or 0.18%. It is considered that the equation reproduces the measured pressures very satisfactorily.

The A function for hydrogen is practically independent of the density, i.e. the value of the constant a is almost zero. However the representation of the experimental data was somewhat better when a negative value was used for this constant. It is believed that this is due to a slight trend in the experimental measurements, and that the value of a for hydrogen should be positive, as it is for all other gases.

It can be seen that the value of b for the monatomic gases is zero. It is of interest to note that the constant a in the Keyes' equation of state was also found³⁵ to be zero for these gases. Although the forms of these two equations of state are quite different, the constant a of Keyes' equation may be considered to correspond approximately to b .

9. USE OF THE EQUATION OF STATE IN THERMODYNAMIC CALCULATIONS.

For the theoretical discussion the most suitable form of the equation of state is

$$p = T\psi(V) - \phi(V) - F(V, T) \quad (A)$$

where

$$\psi(V) = \frac{R}{V^2}[V + B]; \quad B = B_0 \left(1 - \frac{b}{V}\right)$$

$$\phi(V) = \frac{A}{V^2}; \quad A = A_0 \left(1 - \frac{a}{V}\right)$$

$$F(V, T) = \frac{c\psi(V)}{T^2}$$

For use in certain thermodynamic calculations however, the forms (B) and (C) given below, have also been found convenient.

$$p = T\psi(V) - \phi(V) - \frac{\Gamma(V)}{T^2} \quad (B)$$

where

$$\Gamma = c\psi(V)$$

$$p = RT + \frac{\beta}{V} + \frac{\gamma}{V^2} + \frac{\delta}{V^3} \quad (C)$$

where

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0b + A_0a - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

For the calculation of pressures along an isometric or an isothermal, the forms (A) and (C) respectively are the most convenient; and in general for isometric or isothermal calculations these two equations give the desired result most directly.

In some cases where it is desired to keep the temperature and pressure functions separated, the form (B) in which all the functions $\psi(V)$, $\phi(V)$ and $\Gamma(V)$ depend upon volume alone is more suitable.

In a series of papers, the authors propose to use the equation of state presented in the present article, for the calculation of various thermodynamic quantities.

10. SUMMARY.

There is presented a new equation of state for fluids

$$p = \frac{RT(1 - \varepsilon)}{V^2} [V + B] - \frac{A}{V^2} \quad A = A_0 \left(1 - \frac{a}{V} \right)$$

$$B = B_0 \left(1 - \frac{b}{V} \right)$$

$$\varepsilon = \frac{c}{VT^3}$$

which has the desirable properties: (a) ease and uniqueness of determination of the values of the constants for a substance from the experimental pressure-volume-temperature measurements, (b) simplicity of mathematical form, (c) accuracy of representation of the pressure-volume-temperature data over wide ranges of temperature and

density, (*d*) provision for extension of the volume and temperature functions *A*, *B* and ϵ without alteration of the general form of the equation.

A rational basis for this equation of state is presented, using a method introduced by Phillips, which considers that both of the terms *A* and *B* are due to the mutual interactions of the molecules composing a gas. The method is a very general one and does not involve the assumption of any definite law of force. The term ϵ is introduced to take into account the effect of density and temperature on the time of encounter of the molecules.

A summary is given of the general experimental facts known about the isotherms and isometrics of a gas, and the new equation of state is studied from the standpoint of this information. It is shown (1)

that along an isometric the curvature $\left(\frac{\partial^2 p}{\partial T^2}\right)_V$ is always negative, but

approaches zero as the temperature increases or as the density of the isometric decreases, (2) that along an isotherm the pressure

approaches $\frac{RT}{V}$ as the density decreases, but $\left(\frac{\partial p}{\partial V}\right)_T$ at infinitely

low pressures is zero at only one temperature being negative below and positive above this value.

The complete detailed method used for the determination of the values of the constants from any set of pressure-volume-temperature data is given, with the necessary graphs and tables. The data on oxygen is used for this example, which is carried out to a numerical solution for the five adjustable constants *A*₀, *a*, *B*₀, *b*, and *c*. The method is unambiguous, and the values of the constants are uniquely obtained.

The errors produced in the calculation of pressure by small variations of the value of the constants are discussed, and the numerical values given for oxygen.

An extensive bibliography of the compressibility data on the ten gases helium, neon, argon, hydrogen, nitrogen, oxygen, air, carbon dioxide, methane, and ethyl ether is given and critically examined.

In Tables IX to XIX are presented the detailed comparisons of pressures calculated from the equation of state with the observed pressures and the results are summarized in Table XX. The comparison is made at 1777 points for the ten gases with an average deviation of 0.08 atmospheres or 0.18%. It is believed that in most of the cases the consistency of a set of data taken by one observer is

greater than their absolute accuracy, and that the equation of state reproduces the measurements to within the experimental error.

The more convenient forms of the equation of state for thermodynamic calculations are briefly discussed. In future papers, the authors will apply the equation to the high pressure data on gases and liquids, and present the results of the calculations of various experimentally measured thermodynamic quantities.

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11. COMPARISON OF THE OBSERVED WITH THE CALCULATED PRESSURES FOR TEN GASES

TABLE IX.

VALUES OF THE EQUATION OF STATE CONSTANTS FOR TEN GASES.

$$p = \frac{RT(1 - \epsilon)}{V^2} [V + B] - \frac{A}{V^2}$$

$$A = A_0 \left(1 - \frac{a}{V}\right)$$

$$B = B_0 \left(1 - \frac{b}{V}\right)$$

$$\epsilon = \frac{c}{V^2 T^3}$$

Gas	R	Units				Molecular weight.
		Pressure Volume Density Temperature	A ₀	a	b	
He	0.08206	0.0216	0.05984	0.01400	0.0	4.
Ne	0.08206	0.2125	0.02196	0.02060	0.0	20.2
A	0.08206	1.2907	0.02328	0.03931	0.0	39.91
H ₂	0.08206	0.1975	-0.00506	0.02096	-0.04359	0.0504 × 10 ⁴
N ₂	0.08206	1.3445	0.02617	0.05046	-0.00691	4.20 × 10 ⁴
N ₂ *	0.08206	1.1440	0.01788	0.04314	-0.01608	28.016
O ₂	0.08206	1.4911	0.02562	0.04624	0.004208	28.016
Air	0.08206	1.3012	0.01931	0.04611	-0.01101	32.
CO ₂	0.08206	5.0065	0.07132	0.10476	0.07235	28.964
CH ₄	0.08206	2.2769	0.01855	0.05587	-0.01587	44.000
(C ₂ H ₅) ₂ O	0.08206	31.278	0.12426	0.45446	0.11954	16.0308
						74.077

*Values of the constants for Smith and Taylor's data alone.

TABLES X to XIX.

COMPARISON OF THE OBSERVED PRESSURES WITH THOSE CALCULATED FROM
THE EQUATION OF STATE.

See Table IX for the values of the constants and the units used.

For each isotherm the observed pressures are given in the first horizontal line, and the observed minus the calculated pressures in the second. The latter values subtracted from the former give the pressures calculated from the equation of state.

Under the column headed Ref. there is given the reference to the data from which the "observed pressures" were obtained, the following abbreviations being used.

A	Amagat
An	Andrews
B	Beattie
Br	Bartlett
K	Koch
K and B	Keyes and Burks
L	Data from Leiden Laboratory
R	Data from Reichsanstalt (Holborn and Schultze; Holborn and Otto)
S and T	Smith and Taylor
V	Verschoye
W	Witkowski

TABLE X.—HELIUM.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
400	R obs	27.76	55.80	84.13
	obs-calc	-0.05	-0.19	-0.42
300	R obs	23.64	47.53	71.67	96.07
	obs-calc	-0.04	-0.14	-0.31	-0.55
200	R obs	19.52	39.26	59.22	79.41	99.82
	obs-calc	-0.02	-0.09	-0.20	-0.34	-0.53
100.35	L obs	15.41	30.98	46.73	62.67
	obs-calc	-0.02	-0.08	-0.16	-0.27
100	R obs	15.40	30.97	46.73	62.67	78.80	95.11
	obs-calc	-0.01	-0.06	-0.12	-0.21	-0.31	-0.45
50	R obs	13.34	26.83	40.49	54.31	68.30	82.46	96.79
	obs-calc	-0.01	-0.04	-0.08	-0.13	-0.20	-0.27	-0.36
20	L obs	12.10	24.34	36.73	49.26	61.93
	obs-calc	-0.01	-0.03	-0.07	-0.12	-0.20
0	R obs	11.27	22.68	34.23	45.92	57.75	69.72	81.84	94.12
	obs-calc	-0.01	-0.03	-0.05	-0.09	-0.13	-0.18	-0.24	-0.29
0	L obs	11.27	22.68	34.22	45.90	57.71
	obs-calc	-0.01	-0.03	-0.06	-0.11	-0.17
-37.40	L obs	9.73	19.59	29.57	39.67
	obs-calc	-0.01	-0.01	-0.01	-0.03
-50	R obs	9.21	18.54	27.98	37.53	47.20	57.00	66.92	76.97	87.16
	obs-calc	0.00	-0.01	-0.02	-0.04	-0.06	-0.08	-0.10	-0.11	-0.11
-70.32	L obs	8.38	16.86	25.45	34.15	42.96	51.87
	obs-calc	0.00	0.00	0.01	0.01	0.01	0.01
-100	R obs	7.15	14.38	21.70	29.12	36.63	44.23	51.94	59.74	67.64
	obs-calc	0.00	-0.01	-0.01	-0.01	-0.02	-0.02	-0.01	-0.01	0.00
-103.64	L obs	7.00	14.09	21.27	28.54	35.90	43.35	50.89
	obs-calc	0.00	0.01	0.01	0.02	0.03	0.03	0.04
-142.01	L obs	5.41	10.90	16.45	22.08	27.77	33.53	39.36	45.26	51.23
	obs-calc	0.00	0.01	0.01	0.03	0.04	0.06	0.07	0.08	0.08
-150	R obs	5.08	10.23	15.43	20.70	26.03	31.42	36.88	42.41	48.01
	obs-calc	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00
-183	R obs	3.72	7.48	11.28	15.12	19.01	22.95	26.93	30.95	35.02
	obs-calc	0.00	0.00	0.00	-0.01	-0.01	-0.01	-0.01	-0.02	-0.03
-183.32	L obs	3.71	7.46	11.26	15.11	19.00	22.93	26.91	30.94	35.02
	obs-calc	0.00	0.01	0.02	0.04	0.05	0.06	0.07	0.08	0.10
-201.51	L obs	2.95	5.94	8.96	12.02	15.11	18.23	21.39	24.58	27.80
	obs-calc	0.00	0.00	0.00	0.02	0.02	0.02	0.03	0.03	0.02
-205.31	L obs
	obs-calc
-208.0	R obs	2.69	5.40	8.14	10.90	13.70	16.53	19.39	22.29	25.22
	obs-calc	0.00	0.00	0.00	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
-212.06	L obs
	obs-calc
-216.56	L obs	2.33	4.69	7.07	9.48
	obs-calc	0.00	0.00	0.01	0.02

TABLE X.—HELIUM.

[illegible]

TABLE X.—Continued.

Density, moles/liter Temp. °C Ref.	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
	Pressure, atmospheres.								
-217.41 L obs
obs-calc
-225.01 L obs
obs-calc
-252.63 L obs
obs-calc
-252.8 R obs	0.83	1.66	2.49	3.32	4.15	4.98	5.81	6.64	7.48
obs-calc	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01
-258.0 R obs	0.62	1.23	1.83	2.43	3.03	3.62	4.21	4.79	5.38
obs-calc	0.00	0.00	0.00	0.01	0.02	0.03	0.04	0.05	0.07
-258.34 L obs
obs-calc
Average deviation (atm.)	0.009	0.036	0.075	0.103	0.112	0.092	0.086	0.070	0.044
Average % deviation	0.051	0.110	0.153	0.197	0.186	0.153	0.146	0.126	0.098

Note: The values below -252° C are omitted in the averages.

TABLE XI.—NEON.

Density, moles/liter Temp. °C Ref	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
	Pressure, atmospheres.								
400 R obs	27.80	55.99	84.57
obs-calc	-0.05	-0.18	-0.38
300 R obs	23.67	47.67	72.01	96.70
obs-calc	-0.04	-0.12	-0.25	-0.42
200 R obs	19.54	39.33	59.41	79.77	100.42
obs-calc	-0.02	-0.09	-0.16	-0.26	-0.38
100 R obs	15.40	30.99	46.78	62.79	79.02	95.49
obs-calc	-0.01	-0.05	-0.11	-0.16	-0.21	-0.25
20 L obs	12.10	24.33	36.71	49.24	61.93	74.78	87.80	101.00
obs-calc	0.00	-0.01	-0.02	-0.03	-0.04	-0.05	-0.04	-0.03
0 R obs	11.27	22.65	34.17	45.82	57.61	69.54	81.63	93.86	106.26
obs-calc	0.00	-0.02	-0.02	-0.04	-0.05	-0.06	-0.05	-0.06	-0.05
0 L obs	11.26	22.64	34.14	45.77	57.55	69.48	81.58	93.84
obs-calc	-0.01	-0.03	-0.05	-0.09	-0.11	-0.12	-0.10	-0.08
-50 R obs	9.20	18.48	27.85	37.32	46.88	56.55	66.32	76.20	86.19
obs-calc	0.00	0.00	0.00	0.01	0.01	0.03	0.04	0.05	0.07
-100 R obs	7.13	14.30	21.53	28.80	36.14	43.53	50.98	58.49	66.07
obs-calc	0.01	0.01	0.03	0.04	0.07	0.09	0.11	0.13	0.15
-103.01 L obs	6.99	14.01	21.07	28.17	35.33	42.56	49.86	57.24	64.72
obs-calc	-0.01	-0.03	-0.05	-0.08	-0.09	-0.09	-0.08	-0.05	0.02
-141.22 L obs	5.41	10.82	16.24	21.67	27.11	32.58	38.08	43.62	49.20
obs-calc	0.00	-0.01	-0.03	-0.04	-0.06	-0.07	-0.07	-0.06	-0.04
-150 R obs	5.05	10.11	15.17	20.24	25.32	30.41	35.52	40.64	45.78
obs-calc	0.00	0.01	0.02	0.03	0.05	0.06	0.08	0.09	0.10

TABLE X.—Continued.

5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Pressure, atmospheres.										
....	37.09	39.79
....	-0.07	-0.09
....	43.81
....	-0.18
....	12.60	13.46
....	-0.19	-0.23
8.32	9.17	10.01	10.85	11.70	12.55	13.41	14.27	15.14	16.01	16.89
-0.02	-0.02	-0.03	-0.06	-0.08	-0.11	-0.15	-0.19	-0.24	-0.29	-0.36
5.96	6.53	7.10	7.67	8.25	8.83	9.40	9.97	10.54	11.12	11.71
0.08	0.08	0.08	0.08	0.09	0.10	0.10	0.09	0.07	0.06	0.06
....	8.63	9.18	9.72
....	0.17	0.17	0.16
0.036	0.040	0.060	0.083	0.063	0.070	0.088	0.137	0.173	0.065	0.113
0.056	0.075	0.093	0.113	0.103	0.132	0.155	0.163	0.190	0.090	0.207
Total average deviation (atm.)					0.071					
Total average % deviation					0.133					

TABLE XI.—NEON.

[illegible]

TABLE XI.—Continued.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
-182.5	R obs	3.70	7.38	11.03	14.66	18.27	21.85	25.42	28.98	32.52
	obs-calc	0.00	0.01	0.01	0.03	0.04	0.04	0.05	0.06	0.05
-182.6	L obs	3.70	7.37	11.00	14.62	18.21	21.78	25.34	28.88	32.41
	obs-calc	0.00	0.01	0.00	0.00	0.00	0.00	0.00	-0.01	-0.02
-200.08	L obs	2.97	5.90	8.78	11.62	14.42	17.18	19.90	22.59	25.26
	obs-calc	0.00	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01
-207.9	R obs	2.65	5.25	7.79	10.29	12.73	15.13	17.49	19.80	22.08
	obs-calc	0.00	0.01	0.02	0.04	0.04	0.05	0.06	0.06	0.07
-208.10	L obs	2.64	5.22	7.75	10.23	12.66	15.05	17.39	19.68	21.94
	obs-calc	0.00	0.00	0.00	0.01	0.02	0.03	0.03	0.02	0.01
-213.08	L obs	2.43	4.81	7.12	9.38	11.58	13.73	15.83	17.88	19.88
	obs-calc	0.00	0.00	0.01	0.03	0.03	0.04	0.04	0.04	0.04
-217.52	L obs	2.24	4.42	6.53	8.57	10.55	12.47	14.34	16.15	17.91
	obs-calc	-0.01	0.00	0.00	-0.01	-0.02	-0.02	-0.03	-0.04	-0.06
Average deviation (atm.)		0.008	0.032	0.062	0.074	0.073	0.064	0.053	0.053	0.053
Average % deviation		0.070	0.139	0.150	0.187	0.185	0.172	0.153	0.137	0.142

TABLE XII.—Argon.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
400	R obs	27.83	56.09	84.80	113.96
	obs-calc	-0.01	-0.05	-0.11	-0.23
300	R obs	23.65	47.59	71.83	96.42
	obs-calc	0.00	-0.01	-0.04	-0.05
200	R obs	19.46	39.05	58.78	78.70	98.83
	obs-calc	-0.01	-0.02	-0.04	-0.04	-0.02
150	R obs	17.38	34.80	52.29	69.88	87.60	105.46
	obs-calc	0.00	0.00	0.00	0.02	0.05	0.09
100	R obs	15.28	30.52	45.75	60.99	76.26	91.59	107.01
	obs-calc	0.00	-0.01	0.00	0.01	0.03	0.06	0.11
50	R obs	13.19	26.26	39.22	52.10	64.92	77.71	90.48	103.25
	obs-calc	0.00	0.01	0.02	0.02	0.03	0.06	0.08	0.10
20.39	L obs	11.97	23.79	35.46	47.00	58.44
	obs-calc	0.02	0.08	0.14	0.21	0.30
0	R obs	11.09	21.96	32.63	43.13	53.47	63.67	73.77	83.77	93.67
	obs-calc	0.00	-0.01	-0.01	-0.01	-0.02	-0.03	-0.03	-0.03	-0.06
0	L obs	11.10	22.03	32.79	43.34	53.68	63.88
	obs-calc	0.01	0.06	0.15	0.20	0.19	0.18
-50	R obs	8.99	17.65	26.01	34.10	41.92	49.50	56.86	64.02	71.00
	obs-calc	0.00	-0.02	-0.04	-0.05	-0.08	-0.11	-0.14	-0.18	-0.22
-57.72	L obs	8.67	17.04	25.08	32.85	40.38	47.65	54.66	61.42
	obs-calc	0.00	0.04	0.06	0.10	0.17	0.24	0.28	0.28

TABLE XII.—Continued.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
-87.05	L obs	7.42	14.48	21.15	27.44	33.36	39.02	44.34	49.35	54.11
	obs-calc	-0.01	0.02	0.04	0.03	0.00	0.04	0.04	0.02	0.02
-100	R obs	6.88	13.31	19.32	24.92	30.14	35.01	39.55	43.79	47.74
	obs-calc	0.00	-0.03	-0.05	-0.10	-0.15	-0.18	-0.21	-0.21	-0.19
-102.51	L obs	6.76	13.13	19.06	24.57	29.70	34.47	38.88	42.96	46.75
	obs-calc	-0.02	0.01	0.02	0.02	0.01	0.02	0.01	0.00	0.02
-109.88	L obs	6.45	12.48	18.07	23.22	27.94	32.27	36.25	39.89	43.22
	obs-calc	-0.01	0.01	0.03	0.04	0.02	0.00	0.00	0.02	0.07
-113.80	L obs	6.27	12.12	17.50	22.43	26.93	31.03	34.77	38.16	41.23
	obs-calc	-0.03	-0.01	0.00	-0.02	-0.04	-0.07	-0.07	-0.05	0.00
-115.86	L obs	6.18	11.95	17.23	22.04	26.43	30.42	34.04	37.30	40.21
	obs-calc	-0.03	0.00	0.01	-0.02	-0.04	-0.06	-0.05	-0.03	0.00
-116.62	L obs	6.15	11.88	17.11	21.89	26.24	30.19	33.77	36.96	39.80
	obs-calc	-0.03	0.00	-0.01	-0.03	-0.05	-0.06	-0.05	-0.05	-0.04
-119.20	L obs	6.04	11.67	16.78	21.41	25.60	29.35	32.69	35.67	38.32
	obs-calc	-0.03	0.02	0.01	-0.02	-0.06	-0.12	-0.19	-0.23	-0.23
-120.24	L obs	6.00	11.58	16.65	21.24	25.39	29.14	32.50	35.49	38.13
	obs-calc	-0.02	0.02	0.02	0.00	-0.02	-0.02	0.00	0.04	0.09
-121.21	L obs	5.96	11.49	16.53	21.09	25.19	28.85	32.11	35.01	37.58
	obs-calc	-0.02	0.01	0.04	0.04	0.02	-0.01	-0.04	-0.03	0.03
-130.38	L obs	5.58	10.67	15.24	19.31	22.91	26.07	28.80	31.13	33.06
	obs-calc	-0.01	0.01	0.01	0.00	0.00	0.01	0.04	0.10	0.17
-139.62	L obs	5.17	9.83	13.91
	obs-calc	-0.03	-0.01	-0.03
-149.60	L obs	4.74	8.93	12.48
	obs-calc	-0.03	-0.01	-0.05
Average deviation (atm.)		0.013	0.020	0.039	0.057	0.065	0.081	0.084	0.091	0.088
Average % deviation		0.207	0.107	0.147	0.142	0.158	0.174	0.185	0.198	0.195

TABLE XIII.—HYDROGEN.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
200	R obs	19.56	39.44	59.63	80.15	101.02
	obs-calc	-0.01	-0.04	-0.11	-0.24	-0.43
100	R obs	15.43	31.10	47.02	63.21	79.66	96.37
	obs-calc	0.01	0.01	0.00	-0.02	-0.08	-0.21
100	L obs	15.42	31.06	46.93
	obs-calc	0.00	-0.03	-0.09
100	W obs	15.43	31.09	47.01
	obs-calc	0.01	0.00	-0.01
50	R obs	13.36	26.92	40.70	54.69	68.90	83.34	98.01
	obs-calc	0.01	0.02	0.04	0.04	0.01	-0.06	-0.18

TABLE XII.—Continued.

[illegible]

Total average deviation (atm.) 0.078

Total average % deviation	0.203
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TABLE XIII.—HYDROGEN.

[illegible]

TABLE XIII.—Continued.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
20	L obs	12.11	24.40	36.87	49.54	62.42	75.52	88.86
	obs-calc	0.00	0.02	0.03	0.04	0.04	0.03	0.02
0	R obs	11.28	22.73	34.35	46.13	58.09	70.25	82.60	95.15
	obs-calc	0.00	0.03	0.05	0.06	0.05	0.04	0.01	-0.10
0	L obs	11.28	22.71	34.30	46.05
	obs-calc	0.00	0.01	0.00	-0.02
0	W obs	11.28	22.73	34.34	46.12	58.09
	obs-calc	0.00	0.03	0.04	0.05	0.05
-50	R obs	9.21	18.54	27.99	37.56	47.26	57.11	67.10	77.24	87.55
	obs-calc	0.01	0.03	0.05	0.07	0.08	0.09	0.07	0.03	-0.03
-77	W obs	8.09	16.28	24.58	32.98	41.48	50.09	58.82
	obs-calc	0.01	0.03	0.08	0.13	0.16	0.19	0.20
-100	R obs	7.14	14.34	21.62	28.98	36.42	43.94	51.56	59.28	67.10
	obs-calc	0.01	0.02	0.05	0.07	0.10	0.10	0.11	0.10	0.08
-103.55	L obs	6.99	14.04	21.17	28.37	35.65	43.01	50.46	58.02
	obs-calc	0.01	0.02	0.05	0.07	0.10	0.11	0.12	0.13
-104	W obs	6.97	14.02	21.14	28.34	35.62	42.99	50.46	58.02
	obs-calc	0.00	0.04	0.07	0.12	0.17	0.21	0.26	0.29
-139.85	L obs	5.48	11.00	16.55	22.14	27.76	33.43	39.16	44.94
	obs-calc	0.00	0.02	0.05	0.08	0.09	0.11	0.14	0.15
-147	W obs	5.19	10.40	15.64	20.91	26.22	31.58	36.98	42.43	47.94
	obs-calc	0.01	0.02	0.05	0.07	0.11	0.15	0.19	0.22	0.26
-150	R obs	5.06	10.14	15.24	20.37	25.53	30.72	35.95	41.22	46.53
	obs-calc	0.00	0.02	0.03	0.05	0.07	0.08	0.09	0.10	0.08
-164.10	L obs	4.47	8.95	13.44	17.94	22.46	26.99	31.55	36.14
	obs-calc	0.00	0.01	0.03	0.04	0.07	0.08	0.10	0.11
-182.75	L obs	3.70	7.38	11.05	14.70	18.35	22.00	25.65	29.30	32.96
	obs-calc	0.00	0.00	0.01	0.01	0.01	0.02	0.03	0.03	0.02
-183	R obs	3.69	7.37	11.03	14.68	18.32	21.96	25.60	29.24	32.89
	obs-calc	0.00	0.01	0.02	0.03	0.04	0.05	0.05	0.06	0.06
-183	W obs	3.69	7.37	11.04	14.70	18.35	22.01	25.67	29.33	32.99
	obs-calc	0.00	0.01	0.03	0.05	0.07	0.10	0.12	0.15	0.16
-190	W obs	3.40	6.78	10.14	13.48	16.80	20.12	23.43	26.74	30.05
	obs-calc	0.00	0.01	0.03	0.04	0.04	0.06	0.08	0.10	0.11
-195.21	L obs	3.18	6.33	9.46	12.57	15.65	18.72	21.77	24.80	27.83
	obs-calc	0.00	0.00	0.01	0.02	0.03	0.04	0.05	0.05	0.05
-204.63	L obs	2.79	5.54	8.25	10.93	13.57	16.19	18.78	21.34	23.89
	obs-calc	0.00	0.00	0.00	0.01	0.01	0.02	0.02	0.02	0.03
-205	W obs	2.78	5.51	8.21	10.87	13.50	16.10	18.67	21.22	23.74
	obs-calc	0.01	0.00	0.01	0.01	0.02	0.02	0.03	0.04	0.03
-207.9	R obs	2.65	5.26	7.82	10.34	12.83	15.28	17.69	20.08	22.44
	obs-calc	0.00	0.00	-0.01	-0.01	-0.02	-0.02	-0.04	-0.04	-0.06
-212	W obs	2.48	4.91	7.29	9.63	11.94	14.20	16.42	18.61	20.77
	obs-calc	0.00	-0.01	-0.01	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01
-212.74	L obs	2.45	4.85	7.20	9.50	11.76	13.98	16.16	18.31	20.43
	obs-calc	0.00	0.00	-0.01	-0.02	-0.02	-0.03	-0.04	-0.04	-0.04

Pressure, atmospheres.

[illegible]

TABLE XIII.—Continued.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
-217.33	L obs	2.26	4.46	6.61	8.71	10.76	12.75	14.70	16.62	18.50
	obs-calc	0.00	-0.01	-0.01	-0.01	-0.02	-0.03	-0.04	-0.04	-0.04
-225.36	L obs	12.13	13.64
	obs-calc	-0.05	-0.04
-231.39	L obs	10.19	11.38
	obs-calc	-0.04	-0.03
-236.30	L obs	8.59	9.53
	obs-calc	-0.02	0.01
-238.29	L obs	7.95	8.77
	obs-calc	0.01	0.03
-239.91	L obs	7.41	8.16
	obs-calc	0.02	0.06
-241.87	L obs	6.76	7.39
	obs-calc	0.05	0.09
-243.88	L obs	6.08	6.59
	obs-calc	0.07	0.12
Average deviation (atm.)		0.003	0.016	0.034	0.052	0.073	0.078	0.075	0.081	0.071
Average % deviation		0.045	0.108	0.166	0.196	0.215	0.227	0.294	0.355	0.209

TABLE XIV.—NITROGEN.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
400	R obs	27.94	56.59	85.99
	obs-calc	-0.04	-0.14	-0.28
300	R obs	23.76	48.03	72.86	98.29
	obs-calc	-0.02	-0.07	-0.15	-0.25
200	R obs	19.56	39.45	59.71	80.37	101.46
	obs-calc	-0.01	-0.02	-0.04	-0.06	-0.10
150	R obs	17.46	35.16	53.11	71.36	89.94
	obs-calc	0.00	0.00	0.00	-0.01	-0.02
100	R obs	15.36	30.84	46.48	62.31	78.36	94.68
	obs-calc	0.00	0.00	0.00	0.01	0.02	0.04
50	R obs	13.26	26.54	39.87	53.28	66.79	80.43	94.23
	obs-calc	0.01	0.02	0.04	0.06	0.08	0.08	0.08
20	L obs	12.00	23.96	35.88	47.81	59.75
	obs-calc	0.01	0.03	0.04	0.05	0.03
20	V obs	11.99	23.93	35.86	47.80	59.78	71.81	83.91	96.13	108.50
	obs-calc	0.00	0.00	0.02	0.04	0.06	0.06	0.03	-0.01	-0.07
0	R obs	11.15	22.22	33.22	44.18	55.13	66.10	77.11	88.18	99.33
	obs-calc	0.00	0.03	0.05	0.07	0.09	0.10	0.10	0.08	0.03
0	L obs	11.16	22.24	33.23	44.16	55.07
	obs-calc	0.01	0.05	0.06	0.05	0.03

TABLE XIII.—Continued.

[illegible]

Total average deviation (atm.) 0.068

Total average deviation (atm)	0.003
Total average % deviation	0.203

TABLE XIV.—NITROGEN.

[illegible]

TABLE XIV.—Continued.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
0	V obs	11.15	22.20	33.19	44.14	55.08	66.03	77.02	88.08	99.24
	obs-calc	0.00	0.01	0.02	0.03	0.04	0.03	0.01	-0.02	-0.06
0	Br obs	11.16	22.23	33.22	44.16	55.09	66.04	77.02	88.07	99.23
	obs-calc	0.01	0.04	0.05	0.05	0.05	0.04	0.01	-0.03	-0.07
-23.62	L obs	10.15	20.17	30.05	39.83	49.54	59.21	68.87
	obs-calc	0.00	0.02	0.03	0.03	0.03	0.02	0.01
-50	R obs	9.04	17.87	26.50	34.96	43.28	51.48	59.58	67.61	75.59
	obs-calc	0.00	0.01	0.01	-0.01	-0.03	-0.07	-0.13	-0.23	-0.35
-50.26	L obs	9.04	17.88	26.51	34.96	43.26	51.45	59.57
	obs-calc	0.01	0.04	0.05	0.04	0.01	-0.02	-0.05
-81.10	L obs	7.74	15.19	22.37	29.29	35.98	42.47	48.80	54.97	61.00
	obs-calc	0.02	0.04	0.06	0.06	0.04	0.01	-0.02	-0.07	-0.16
-100	R obs	6.92	13.50	19.76	25.71	31.39	36.82	42.01	47.01	51.82
	obs-calc	0.00	0.00	0.00	-0.01	-0.02	-0.04	-0.08	-0.13	-0.19
-102.25	L obs	6.83	13.31	19.47	25.33	30.91	36.22	41.29	46.16	50.85
	obs-calc	0.00	0.01	0.02	0.03	0.04	0.03	0.00	-0.02	-0.06
-121.19	L obs	6.03	11.65	16.89	21.75	26.26	30.46	34.38	38.05	41.48
	obs-calc	0.01	0.01	0.02	0.02	-0.01	-0.02	-0.03	-0.02	-0.01
-130	R obs	5.65	10.85	15.63	20.01	24.02	27.69	31.04	34.09	36.88
	obs-calc	0.00	-0.01	-0.02	-0.05	-0.07	-0.09	-0.11	-0.13	-0.12
-131.27	L obs	5.59	10.70	15.41	19.74	23.73	27.38	30.70	33.71	36.45
	obs-calc	0.00	-0.04	-0.07	-0.07	-0.05	-0.01	-0.03	0.06	0.10
-141.53	L obs	5.16	9.84	14.05	17.81	21.16	24.14	26.78	29.12	31.16
	obs-calc	0.01	0.01	0.00	-0.02	-0.05	-0.05	-0.01	0.07	0.18
-144.46	L obs	5.03	9.56	13.62	17.23	20.42	23.22	25.66	27.78	29.60
	obs-calc	0.00	-0.01	-0.02	-0.03	-0.04	-0.04	-0.01	0.07	0.19
-146.32	L obs	4.94	9.38	13.34	16.86	19.95	22.64	24.96	26.94	28.62
	obs-calc	-0.01	-0.02	-0.04	-0.04	-0.04	-0.03	0.01	0.08	0.20
-148.58	L obs	4.85	9.20	13.07	16.47	19.43	21.98	24.14	25.93	27.41
	obs-calc	0.00	0.00	0.01	0.01	0.02	0.04	0.07	0.12	0.22
Average deviation (atm.)		0.006	0.026	0.044	0.046	0.042	0.043	0.044	0.076	0.134
Average % deviation		0.062	0.118	0.134	0.113	0.110	0.106	0.098	0.187	0.318

TABLE XIV.—A

Data of Smith and Taylor Compared with Special Equation Based on Their Measurements

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
		Pressure, atmospheres.							
200	S + T obs	19.55	39.40	59.58	80.10	101.00	122.32	144.10	166.39
	obs-calc	0.00	0.02	0.04	0.03	0.02	0.00	-0.03	-0.05
152.34	S + T obs	17.55	35.31	53.30	71.55	90.09	108.95	128.18	147.83
	obs-calc	0.00	0.02	0.02	0.03	0.02	0.00	-0.01	0.00
100	S + T obs	15.36	30.83	46.43	62.19	78.13	94.29	110.70	127.40
	obs-calc	0.01	0.03	0.04	0.05	0.05	0.05	0.05	0.05

TABLE XIV.—Continued.

5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Pressure, atmospheres.										
110.54	122.01
-0.11	-0.16
110.57	122.13
-0.08	-0.04
....
....
83.55	91.54
-0.50	-0.66
....
....
....
....
56.47	61.00
-0.27	-0.35
55.38
-0.10
44.66	47.60
-0.03	-0.10
39.44	41.83
-0.10	-0.10
38.95	41.22
0.16	0.24
32.91	34.41
0.31	0.47
31.15	32.42
0.36	0.55
30.00	31.11
0.36	0.56
28.61	29.56
0.39	0.63
0.222	0.324
0.532	0.779

Total average deviation (atm.) 0.072

Total average % deviation 0.190

TABLE XIV.—A

4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Pressure, atmospheres.											
189.24	212.70	236.84	261.74	287.45	314.04
-0.04	0.01	0.13	0.38	0.77	1.33
167.95	188.58	209.77	231.57	254.03	277.18
0.05	0.15	0.31	0.56	0.91	1.36
144.44	161.85	179.67	197.96	216.75	236.07
0.08	0.13	0.23	0.39	0.62	0.92

TABLE XIV.—A—Continued.

Density, moles/liter Temp. °C Ref.			0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
			Pressure, atmospheres.							
49.98	S + T	obs	13.25	26.51	39.80	53.14	66.55	80.08	93.76	107.65
		obs-calc	0.00	0.00	0.00	-0.01	-0.04	-0.06	-0.08	-0.06
0	S + T	obs	11.16	22.22	33.21	44.15	55.06	65.96	76.90	87.91
		obs-calc	0.01	0.01	0.01	0.01	0.00	-0.03	-0.05	-0.05
Average deviation (atm.)			0.004	0.016	0.022	0.026	0.026	0.028	0.044	0.042
Average % deviation			0.032	0.052	0.046	0.040	0.032	0.034	0.044	0.038

TABLE XV.—OXYGEN.

Density, moles/liter Temp. °C Ref.			0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
			Pressure, atmospheres.								
100	R	obs	15.29	30.54	45.78	61.03	76.31	91.64
		obs-calc	0.00	-0.01	-0.02	-0.04	-0.07	-0.12
50	R	obs	13.19	26.26	39.22	52.10	64.91	77.67	90.41	103.14
		obs-calc	0.00	0.01	0.02	0.03	0.02	0.00	-0.03	-0.09
20	L	obs	11.93	23.67	35.25	46.68	57.97
		obs-calc	0.00	0.01	0.02	0.02	0.00
0	R	obs	11.09	21.95	32.61	43.09	53.42	63.59	73.64	83.58	93.43
		obs-calc	0.01	0.01	0.03	0.04	0.07	0.07	0.06	0.04	-0.02
0	L	obs	11.09	21.95	32.61	43.09	53.39
		obs-calc	0.01	0.01	0.03	0.04	0.04
-40.05	L	obs	9.40	18.48	27.27	35.79	44.06	52.10	59.97
		obs-calc	0.00	0.00	0.00	0.00	0.00	-0.01	0.01
-80.03	L	obs	7.71	15.01	21.92	28.47	34.69	40.60	46.21	51.54	56.60
		obs-calc	0.00	0.00	-0.01	-0.01	0.00	0.02	0.03	0.04	0.03
-102.46	L	obs	6.77	13.07	18.93	24.35	29.36	33.98	38.25	42.21	45.86
		obs-calc	0.01	0.01	0.02	0.02	0.01	-0.02	-0.04	-0.03	-0.02
-109.97	L	obs	6.45	12.41	17.90	22.94	27.54	31.74	35.58	39.07	42.23
		obs-calc	0.01	0.01	0.01	0.01	-0.01	-0.03	-0.02	-0.01	0.00
-113.98	L	obs	6.28	12.06	17.35	22.17	26.55	30.51	34.10	37.33	40.21
		obs-calc	0.01	0.01	0.01	-0.01	-0.03	-0.06	-0.06	-0.06	-0.05
-116.01	L	obs	6.19	11.87	17.05	21.77	26.04	29.89	33.37	36.49	39.25
		obs-calc	0.00	0.00	-0.01	-0.03	-0.05	-0.07	-0.06	-0.03	-0.01
-116.99	L	obs	6.15	11.79	16.93	21.60	25.81	29.60	33.00	36.03	38.72
		obs-calc	0.00	0.01	0.00	-0.01	-0.04	-0.06	-0.07	-0.07	-0.05
Average deviation (atm.)			0.004	0.008	0.015	0.022	0.028	0.046	0.042	0.046	0.026
Average % deviation			0.054	0.044	0.056	0.063	0.070	0.109	0.102	0.094	0.056

TABLE XVI.—AIR.

Density, moles/liter Temp. °C Ref.		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
		Pressure, atmospheres.								
200	R obs	19.53	39.33	59.44	79.90	100.73
	obs-calc	-0.01	-0.01	-0.01	0.01	0.02
150	R obs	17.44	35.05	52.88	70.95	89.30	107.97
	obs-calc	0.00	0.01	0.03	0.05	0.09	0.16
100	R obs	15.34	30.77	46.30	61.98	77.84	93.92	110.25
	obs-calc	0.00	0.03	0.05	0.09	0.14	0.23	0.35
100	W obs	15.33	30.70	46.17	61.78	77.57	93.56	109.78	126.26
	obs-calc	-0.01	-0.04	-0.08	-0.11	-0.13	-0.13	-0.12	-0.10
50	R obs	13.24	26.47	39.70	52.97	66.30	79.72	93.25	106.94
	obs-calc	0.01	0.03	0.05	0.09	0.14	0.19	0.24	0.31
20	L obs	11.99	23.89	35.73	47.51	59.27
	obs-calc	0.02	0.03	0.05	0.05	0.04
16	W,A obs	11.80	23.50	35.11	46.66	58.20	69.77	81.37	93.03	104.80
	obs-calc	-0.01	-0.01	0.06	-0.07	-0.10	-0.11	-0.12	-0.13	-0.11
0	R obs	11.14	22.15	33.06	43.90	54.69	65.46	76.21	86.98	97.80
	obs-calc	0.01	0.02	0.03	0.06	0.09	0.13	0.16	0.19	0.21
0	W obs	11.14	22.14	33.02	43.81	54.54	65.26	75.99	86.75	97.58
	obs-calc	0.01	0.01	-0.01	-0.03	-0.06	-0.07	-0.06	-0.04	-0.01
0	K obs	11.12	22.09	32.94	43.71	54.42	65.11	75.81	86.54	97.33
	obs-calc	-0.01	-0.04	-0.09	-0.13	-0.18	-0.22	-0.24	-0.25	-0.26
-35	W obs	9.67	19.15	28.44	37.57	46.56	55.44	64.23	72.95	81.61
	obs-calc	0.01	0.04	0.06	0.08	0.10	0.12	0.13	0.14	0.13
-70.09	L obs	51.92	58.58
	obs-calc	-0.07	-0.04
-78.5	W obs	7.84	15.37	22.62	29.60	36.33	42.84	49.15	55.27	61.21
	obs-calc	0.01	0.03	0.05	0.06	0.07	0.08	0.09	0.09	0.06
-79.1	K obs	7.79	15.26	22.43	29.34	36.02	42.47	48.72	54.78	60.69
	obs-calc	-0.01	-0.03	-0.06	-0.09	-0.10	-0.12	-0.13	-0.16	-0.17
-84.08	L obs	47.04	52.77	58.33
	obs-calc	-0.07	-0.12	-0.17
-103.48	L obs	40.13	44.68	48.99
	obs-calc	-0.13	-0.16	-0.19
-103.5	W obs	6.77	13.17	19.22	24.92	30.29	35.36	40.16	44.72	49.06
	obs-calc	0.00	0.01	0.01	0.00	-0.03	-0.06	-0.09	-0.11	-0.11
-122.03	L obs	33.45	36.81	39.91
	obs-calc	-0.13	-0.15	-0.13
-129.97	L obs	30.50	33.35	35.93
	obs-calc	-0.16	-0.16	-0.10
-134.99	L obs	28.61	31.13	33.35
	obs-calc	-0.18	-0.17	-0.11
-140.00	L obs	26.70	28.88	30.75
	obs-calc	-0.21	-0.19	-0.10
-145.05	L obs	24.74	26.56	28.05
	obs-calc	-0.24	-0.22	-0.13
Average deviation (atm.)		0.009	0.024	0.046	0.066	0.092	0.135	0.154	0.152	0.133
Average % deviation		0.078	0.113	0.139	0.148	0.164	0.204	0.327	0.308	0.251

TABLE XVII.—CARBON DIOXIDE.

Density, moles/liter Temp. °C Ref.	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
	Pressure, atmospheres.								
100 A obs	14.78	28.53	41.32	53.22	64.32	74.72	84.50	93.72	102.43
obs-calc	0.01	0.01	0.02	0.01	0.01	0.04	0.08	0.10	0.06
100 An obs	14.75	28.47	41.28	53.30	64.57	75.06	84.86	94.45	103.19
obs-calc	-0.02	-0.05	-0.02	0.09	0.26	0.38	0.44	0.83	0.82
90 A obs	14.34	27.61	39.86	51.16	61.61	71.32	80.39	88.86	96.80
obs-calc	0.00	0.02	0.02	-0.01	-0.04	-0.05	-0.03	-0.05	-0.12
80 A obs	13.89	26.64	38.33	49.06	58.93	68.04	76.46	84.23	91.41
obs-calc	-0.01	-0.03	-0.05	-0.06	-0.05	0.00	0.06	0.07	-0.02
70 A obs	13.45	25.69	36.86	47.04	56.32	64.77	72.47	79.50	85.92
obs-calc	-0.01	-0.05	-0.05	-0.03	0.03	0.09	0.13	0.13	0.05
63.75 An obs	13.18	25.17	36.10	46.04	55.10	63.33	70.80	77.53	83.66
obs-calc	-0.01	0.01	0.11	0.26	0.50	0.76	1.02	1.18	1.29
60 A obs	13.01	24.78	35.41	45.01	53.66	61.44	68.42	74.67	80.27
obs-calc	-0.01	-0.03	-0.03	0.01	0.07	0.14	0.18	0.15	0.01
50 A obs	12.58	23.86	33.94	42.93	50.93	58.03	64.28	69.77	74.59
obs-calc	0.00	-0.01	-0.01	0.01	0.07	0.14	0.18	0.14	0.02
48.1 An obs	64.11	69.62	74.42
obs-calc	0.80	0.93	0.94
40 A obs	12.15	22.94	32.48	40.86	48.19	54.58	60.09	64.79	68.78
obs-calc	0.01	0.00	0.01	0.03	0.07	0.14	0.17	0.12	-0.03
35.5 An obs	58.12	62.52	66.29
obs-calc	0.10	0.11	0.10
35 A obs	11.92	22.45	31.71	39.80	46.81	52.85	59.00	62.32	65.91
obs-calc	0.00	-0.02	-0.01	0.03	0.08	0.14	0.19	0.16	0.02
32.5 An obs	56.93	61.07	64.48
obs-calc	0.18	0.17	0.06
32 A obs	11.79	22.21	31.32	39.22	46.02	51.83	56.75	60.83	64.15
obs-calc	0.00	0.03	0.05	0.08	0.12	0.17	0.21	0.18	0.02
31.1 An obs	45.53	51.36	56.29	60.37	63.72
obs-calc	-0.12	0.02	0.14	0.17	0.12
30 A obs	11.69	21.95	30.92	38.70	45.39	51.08	55.84	59.76	62.93
obs-calc	-0.01	-0.05	-0.05	-0.02	0.05	0.12	0.16	0.12	-0.02
20 A obs	11.26	21.03	29.43	36.56	42.54	47.49	51.49	54.57
obs-calc	0.00	-0.02	-0.03	-0.03	0.00	0.06	0.10	0.04
10 A obs	10.82	20.10	27.89	34.33	39.58	43.80
obs-calc	0.00	0.00	-0.05	-0.11	-0.13	-0.06
6.5 An obs	10.63	19.76	27.48	33.86
obs-calc	-0.03	-0.01	0.08	0.18
0 A obs	10.38	19.15	26.39	32.19
obs-calc	0.01	0.01	-0.02	-0.08
Average deviation (atm.)	0.007	0.021	0.034	0.050	0.065	0.090	0.136	0.122	0.050
Average % deviation	0.060	0.088	0.108	0.131	0.136	0.163	0.224	0.184	0.066

Note: The 100°, 63.75°, and 48.1° isotherms of Andrews show large variations from Amagat's data, and hence are excluded in the averages.

TABLE XVIII.—METHANE.

Density, moles/liter Temp. °C Ref.			0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
			Pressure, atmospheres.							
200	K + B	obs	19.39	38.77	58.18	77.66	97.26	117.06	137.11	157.46
		obs-calc	0.01	0.03	0.04	0.04	0.01	-0.02	-0.05	-0.09
150	K + B	obs	17.28	34.42	51.46	68.44	85.42	102.47	119.63	136.94
		obs-calc	0.01	0.02	0.03	0.02	0.00	-0.01	-0.03	-0.07
100	K + B	obs	15.16	30.06	44.74	59.23	73.59	87.85	102.08	116.32
		obs-calc	0.00	0.02	0.04	0.04	0.04	0.02	-0.01	-0.04
50	K + B	obs	13.04	25.69	37.98	49.94	61.62	73.08	84.35	95.49
		obs-calc	0.00	0.01	0.02	0.01	0.00	-0.02	-0.04	-0.06
0	K + B	obs	10.92	21.29	31.16	40.56	49.53	58.13	66.41	74.40
		obs-calc	0.00	-0.01	-0.02	-0.03	-0.06	-0.07	-0.06	-0.04
Average deviation (atm.)			0.004	0.018	0.030	0.028	0.022	0.028	0.038	0.060
Average % deviation			0.022	0.060	0.066	0.048	0.036	0.040	0.044	0.050

TABLE XVIII.—METHANE.

4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Pressure, atmospheres.											
178.18	199.36	221.09	243.46
-0.13	-0.12	-0.05	0.14
154.46	172.27	190.45	209.08
-0.11	-0.13	-0.10	0.00
130.64	145.09	159.74	174.62
-0.06	-0.06	-0.03	0.02
106.56	117.60	128.64	139.71
-0.05	-0.03	-0.01	0.01
82.16	89.73	97.10	104.23
0.02	0.11	0.19	0.17
0.074	0.090	0.076	0.068
0.052	0.066	0.060	0.048

Total average deviation (atm.) 0.045

Total average % deviation 0.049

TABLE XX

SUMMARY OF THE AVERAGE DEVIATION OF THE PRESSURES CALCULATED
BY THE EQUATION OF STATE FROM THE OBSERVED PRESSURES

See Tables IX to XIX

Gas	Maximum Pressure (Atmospheres)	Maximum Density (Moles/liter)	Temperature range (Degrees C.)	Number of Points	Total Average Deviation Atmospheres	Deviation %
He	102	10	400 to -252	183	0.071	0.133
Ne	106	8.5	400 to -217	229	0.081	0.209
A	114	6	400 to -150	209	0.078	0.203
H ₂	103	10	200 to -244	362	0.068	0.203
N ₂ *	134	5.5	400 to -149	214	0.072	0.190
O ₂	103	9	100 to -117	137	0.051	0.115
Air	177	8	200 to -145	171	0.113	0.198
CO ₂	111	5.5	100 to 0	148	0.128	0.203
CH ₄	243	6	200 to 0	60	0.045	0.049
(C ₂ H ₅) ₂ O	90	2.7	325 to 150	64	0.023	0.076
Grand Average					0.077	0.178

* The comparisons of the data of Smith and Taylor with the special equation based on their measurements alone are not included. To do so would reduce the deviations given in this table.

12. BIBLIOGRAPHY OF THE COMPRESSIBILITY DATA ON TEN GASES

SOURCES OF THE PRESSURE-VOLUME-TEMPERATURE DATA CONSIDERED IN
THE COMPUTATION OF TABLES X TO XIX.

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
<i>Helium</i>			
Ramsay and Travers	Zeit. für Phys. Chem., 38, 641 (1901); Phil. Trans., 197(A), 47 (1901).	237.3	54-102
		11.2	28-101
K. Onnes	Leiden Comm., 102a; Verslag Akad. Amsterdam, Dec. 1907, p. 495.	100.35	43-67
		20	28-54
		0	27-50
		-103.57	21-33
		-182.75	14-18
K. Onnes	Leiden Comm., 102c; Verslag Akad. Amsterdam, March, 1908, p. 741.	-216.56	10-11
		-252.72	54-66
		-258.82	40-53
Martinez and K. Onnes	Leiden Comm., 164; Archives Néerlandaises, III A, 6, 253 (1923).	-252.6	0.1-0.8
Penning and K. Onnes	Leiden Comm., 165 c, 166; Archives Néerlandaises, III A, 7, 166, 172 (1923).	-205.31	44-50
		-212.06	40-45
		-217.41	36-41
		-252.65	12-14
		-258.34	9-10
Boks and K. Onnes	Leiden Comm., 170 a; Fourth Int. Cong. Refrig., London, June, 1924.	20	27-63
		0	27-59
		-37.40	24-47
		-70.32	23-56
		-103.64	21-50
		-142.01	21-53
		-183.32	21-37
		-201.51	20-30
		-225.01	43-55
		-235.91	37-55
		-249.87	25-33
		-252.63	23-28
		-256.04	19-22
K. Onnes and Boks	Leiden Comm., 170 b; Fourth Int. Cong. Refrig., London, June 1924.	-258.78	15-18
		-268.88	<1
		-269.37	<1
		-269.69	<1
		-270.52	<1
van Agt and K. Onnes	Leiden Comm., 176b; Verslag Akad. Amsterdam, June 1925, p. 625.	69.86° K	<1
		20.55° K	<1
		20.53° K	<1
		20.51° K	<1
		16.65° K	<1

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
Holborn and Schultze	Ann. der Physik, 47, 1089 (1915).	100	20-50
		50	25-47
		0	25-50
Holborn and Otto	Zeit. für Physik, 10, 367 (1922).	100	20-100
		50	25-99
		0	25-98
✓ Holborn and Otto	Zeit. für Physik, 30, 320 (1924).	-50	23-98
		-100	19-98
		-150	25-98
		-183	20-72
Holborn and Otto	Zeit. für Physik, 23, 77 (1924); Wiss. Abh. Phys. Tech. Reich., 8 (I), 41 (1924).	400	26-98
		300	75
		200	23-99
✓ Holborn and Otto	Zeit. für Physik, 33, 1 (1925); Wiss. Abh. Phys. Tech. Reich., 9 (I), 163 (1925).	{ 400 to -183	0-100
		Smoothed	values
✓ Holborn and Otto	Zeit. für Physik, 38, 359 (1926).	-183	51-98
		-208	26-98
		-252.8	12-98
		-258	12-98
Bridgman	Proc. Nat. Acad. Sci., 9, 370 (1923); Proc. Amer. Acad. Arts and Sci., 59, 173 (1924).	95	3900-20000
		65	3900-20000
		30	3900-20000
Neon			
Ramsay and Travers	Zeit. für Phys. Chem., 38, 641 (1901); Phil. Trans., 197 (A), 47 (1901).	237.3	44-94
		11.2	39-94
✓ K. Onnes and Crommelin	Leiden Comm., 147 d; Verslag Akad. Amsterdam, June 1915, p. 392.	20	23-93
		0	22-85
		-182.6	67-79
		-200.1	62-80
		-208.1	58-79
		-213.1	54-80
✓ Crommelin, Martinez and K. Onnes	Leiden Comm., 154 a; Verslag Akad. Amsterdam, March 1919, p. 1316.	-217.5	50-79
		20	23-93
		0	22-85
		-103.01	36-78
		-141.22	34-79
		-182.60	32-63
Holborn and Otto	Zeit. für Physik, 23, 77 (1924); Wiss. Abh. Phys. Tech. Reich., 8 (I), 41 (1924).	-200.08	26-80
		-208.10	24-79
		-213.08	23-80
		-217.52	21-79
		400	26-99
		300	26-99
✓ Holborn and Otto	Zeit. für Physik, 33, 1 (1925); Wiss. Abh. Phys. Tech. Reich., 9 (I), 163 (1925).	200	23-98
		100	24-99
		0	25-99
		400	27-98
		300	26-99
		200	22-99

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
		100	39-99
		0	25-99
		-50	22-99
		-100	25-99
		-150	24-98
		-182.5	20-73
		{ 400 to -182.5	0-100
		Smoothed values	
Holborn and Otto	Zeit. für Physik, 38, 359 (1926).	-207.9	20-89
<i>Argon</i>			
Ramsay and Travers	Zeit. für Phys. Chem., 38, 641 (1901); Phil. Trans., 197 (A), 47 (1901).	237.3 11.2	43-103 30-101
K. Onnes and Crommelin	Leiden Comm., 118 b; 120 a; 121 b; 128; Verslag. Akad. Amsterdam, Oct. 1910, p. 582; Feb. 1911, p. 1177; May 1911, p. 68; June 1912, p. 256.	20.39 18.39 0 -57.72 -87.05 -102.51 -109.88 -113.80 -115.86 -116.62 -119.20 -120.24 -121.21 -130.38 -139.62 -149.60	22-62 37-62 21-62 18-62 16-62 15-62 14-60 31-59 31-62 14-61 14-54 31-53 14-51 13-33 12-15 11-13
Holborn and Schultze	Ann. der Physik, 47, 1089 (1915).	200 150 100 50 0	24-99 21-98 20-98 25-98 25-98
Holborn and Otto	Zeit. für Physik, 23, 77 (1924); Wiss. Abh. Phys. Tech. Reich., 8 (I), 41, 1924.	400 300	26-100 26-99
Holborn and Otto	Zeit. für Physik, 30, 320 (1924).	-50 -100	20-99 23-74
Holborn and Otto	Zeit. für Physik, 33, 1 (1925); Wiss. Abh. Phys. Tech. Reich., 9 (I), 163 (1925).	{ 400 to -100 Smoothed	0-100 values
Bridgman	Proc. Nat. Acad. Sci., 9, 370 (1923); Proc. Amer. Acad. Arts and Sci., 59, 173 (1924).	55	2600-20000
Masson and Dolley	Proc. Roy. Soc., London, 103A, 524 (1923)	24.95	5-125
<i>Hydrogen</i>			
Amagat	Ann. Chim. Phys., (5), 19, 345 (1880).	20 ±	32-400

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
Amagat	Ann. Chim. Phys., (5), 22, 353 (1881).	100.1	39-420
		81.1	39-420
		60.4	39-420
		40.4	39-420
		17.7	39-420
Amagat	Compt. Rend., 107, 522 (1888).	15	1000-3000
		47	1000-3000
Amagat	Ann. Chim. Phys., (6), 29, 68 (1893).	200.25	150-900
		99.25	150-1000
		15.5	100-1000
		0	100-1000
		47.3	1000-2900
		15.4	700-3000
Wroblewski	Monat. für Chem., 9, 1067 (1888); Wien. Ber., 97 II A, 1321 (1889).	0	100-2800
		99.14	30-71
		0	30-71
		-103.55	20-71
		-182.45	15-71
Schalkwijk	Leiden Comm., 70; Verslag Akad. Amsterdam, June 1901.	20	6-60
K. Onnes and Hyndman	Leiden Comm., 78 c; Verslag Akad. Amsterdam, March 1902.	20	48-56
		0	45-53
K. Onnes and Braak	Leiden Comm., 97 a; Verslag Akad. Amsterdam, Dec. 1906 p. 517.	-103.57	32-50
		-135.71	29-33
		-182.81	47-55
		-195.27	41-50
		-204.70	35-62
		-212.82	31-61
		-212.98	30-35
		-217.41	46-59
		-103.57	28-58
K. Onnes and Braak	Leiden Comm., 99 a; 100 a; Verslag Akad. Amsterdam, June 1907, p. 162; Nov. 1907, p. 441.	-139.88	25-48
		-164.14	23-40
		-182.81	20-32
		-195.17	19-28
		-204.70	17-24
		-212.82	15-21
		-217.41	15-19
		100	31-50
K. Onnes and Braak	Leiden Comm., 100 b; Verslag Akad. Amsterdam, Nov. 1907, p. 420.	0	27-51
K. Onnes and Braak	Leiden Comm., 101 b; Verslag Akad. Amsterdam, Nov. 1907, p. 420.	Correction to tempera- tures of preceding articles.	
de Haas	Leiden Comm., 127 a; Verslag Akad. Amsterdam, April 1912, p. 1422.	20	0.1-1.1
K. Onnes and de Haas	Leiden Comm., 127 c; Verslag Akad. Amsterdam, May 1912, p. 92; June 1912, p. 282.	-252.63	<1
		-255.46	<1
		-257.26	<1

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
K. Onnes, Dorsman and Holst	Leiden Comm., 146 a; Verslag Akad. Amsterdam, June 1915, p. 344.	20	67-90
K. Onnes, Crommelin and Smid	Leiden Comm., 146 b; Verslag Akad. Amsterdam, June 1915, p. 350.	20	65-100
Martinez and K. Onnes	Leiden Comm., 164; Archives Néerlandaises, III A, 6, 253 (1923).	-252.6	< 1
K. Onnes and Penning	Leiden Comm., 165 b; 166; Ar- chives Néerlandaises, III A, 7, 157 (1913); <i>ibid</i> , III A, 7, 172 (1923).	-103.57 -139.89 -182.74 -203.96 -212.73 -217.32 -225.37 -231.38 -236.28 -238.29 -239.90 -241.87 -243.88	38-51 30-40 20-30 17-22 15-18 13-17 10-14 9-11 8-9 8-9 7-8 6-7 6-7
Crommelin and Swallow	Leiden Comm., 172 a; Fourth Int. Cong. Refrig., London, June 1924	-217.33 -225.36 -231.40 -236.31 -238.29 -239.92	34-57 28-56 23-49 18-40 15-46 13-51
van Agt and K. Onnes	Leiden Comm., 176 b; Verslag Akad. Amsterdam, June 1925, p. 625.	90.23° K 69.86° K 20.55° K 20.53° K 20.51° K 20.49° K 18.16° K 16.65° K 15.64° K 14.50° K	< 1 < 1 < 1 < 1 < 1 < 1 < 1 < 1 < 1 < 1
Witkowski	Krakauer Anzeiger, 305 (1905); Landolt-Börnstein Tabellen, I, (1923), p. 105.	100 0 -77 -104 -147 -183 -190 -205 -212	5-60 5-60 5-60 5-60 5-60 5-60 5-60 5-60 5-60
Konstamm and Walstra	Proc. Roy. Acad. Amsterdam, 17, 203 (1914).	20 15.5	124-2280 136-2260
Holborn	Ann. der Phys., 63, 674 (1920)	100 50 0	20-99 25-96 25-97

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
		$\begin{cases} 100-0 \\ \text{Smoothed} \end{cases}$ 200	$\begin{cases} 0-100 \\ \text{values} \end{cases}$ 22-100
Holborn and Otto	Zeit. für Physik, 23, 77 (1924); Wiss. Abh. Phys. Tech. Reich., 8 (I), 41 (1924).		
Holborn and Otto	Zeit. für Physik, 33, 1 (1925) Wiss. Abh. Phys. Tech. Reich., 9 (I), 163 (1925).	$\begin{cases} -50 \\ -100 \\ -150 \\ -183 \end{cases}$	$\begin{cases} 21-98 \\ 27-99 \\ 25-99 \\ 25-75 \end{cases}$
Holborn and Otto	Zeit. für Physik, 38, 359 (1916).	$\begin{cases} 200 \text{ to } -183 \\ \text{Smoothed} \end{cases}$	$\begin{cases} 0-100 \\ \text{values} \end{cases}$
Verschöyle	Proc. Roy. Soc. London, 111 A, 552 (1926).	$\begin{cases} -207.9 \\ 20 \\ 0 \end{cases}$	$\begin{cases} 20-98 \\ 46-205 \\ 46-205 \end{cases}$
Bartlett	Jour. Am. Chem. Soc., 49, 687 (1927); <i>ibid.</i> , 49, 1955 (1927)	0	50-1000
Bridgman	Proc. Nat. Acad. Sci., 9, 370 (1923); Rec. trav. Chim., 42, 568 (1923). Proc. Amer. Acad. Arts and Sci., 59, 173 (1924)	$\begin{cases} 65 \\ 30 \end{cases}$	$\begin{cases} 3900-17000 \\ 2600-17000 \end{cases}$
<i>Nitrogen</i>			
Amagat	Ann. Chim. Phys., (5), 19, 345 (1880); Compt. Rend., 88, 336 (1879).	20 \pm	27-431
Amagat	Ann. Chim. Phys., (5), 22, 353 (1881).	$\begin{cases} 100.1 \\ 75.5 \\ 50.4 \\ 30.1 \end{cases}$	$\begin{cases} 39-420 \\ 39-420 \\ 39-420 \\ 39-420 \end{cases}$
Amagat	Compt. Rend., 99, 1017, 1153 (1884).	$\begin{cases} 17.7 \\ 16 \end{cases}$	$\begin{cases} 39-420 \\ 26-85 \end{cases}$
Amagat	Compt. Rend., 107, 522 (1888).	15	750-3000
Amagat	Ann. Chim. Phys., (6), 29, 68 (1893).	$\begin{cases} 199.50 \\ 99.45 \\ 16.03 \\ 0 \\ 43.6 \\ 16 \\ 0 \end{cases}$	$\begin{cases} 150-950 \\ 150-950 \\ 100-1000 \\ 100-1000 \\ 900-3000 \\ 800-3000 \\ 100-3000 \end{cases}$
Ramsay and Travers	Zeit. für Phys. Chem. 38, 641 (1901); Phil. Trans., 197 (A), 47 (1901).	$\begin{cases} 237.3 \\ 11.2 \end{cases}$	$\begin{cases} 51-101 \\ 55-104 \end{cases}$
Holborn and Otto	Zeit. für Physik, 10, 367 (1922).	$\begin{cases} 100 \\ 50 \\ 0 \end{cases}$	$\begin{cases} 19-99 \\ 25-99 \\ 25-99 \end{cases}$
Holborn and Otto	Zeit. für Physik, 23, 77 (1924); Wiss. Abh. Phys. Tech. Reich., 8 (I), 41 (1924).	$\begin{cases} 400 \\ 300 \\ 200 \\ 150 \\ 100 \end{cases}$	$\begin{cases} 26-99 \\ 26-99 \\ 23-97 \\ 21-98 \\ 19-99 \end{cases}$

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
		50	50-97
		0	25-98
Holborn and Otto	Zeit. für Physik., 30, 320 (1924).	0	100
		-50	20-99
		-100	25-98
		-130	21-67
Holborn and Otto	Zeit. für Physik, 33, 1 (1925); Wiss. Abh. Phys. Tech. Reich., 9 (I), 163 (1925).	400 to -130 Smoothed	0-100 values
Smith and Taylor	Jour. Am. Chem. Soc., 45, 2107 (1923); <i>ibid.</i> , 48, 3122 (1926).	200 152.34 100 49.98 0	61-320 55-282 48-240 41-200 34-160
K. Onnes and van Urk	Leiden Comm., 169 d; 169 e; Fourth Int. Cong. Refrig. London, June 1924.	20 0 -23.62 -50.26 -81.10 -102.25 -121.19 -131.27 -141.53 -144.46 -146.32 -148.58	36-63 33-59 33-61 32-57 30-57 28-55 27-54 25-58 24-50 23-42 23-36 23-31
Verschoye	Proc. Roy. Soc. London, 111 A, 552 (1926).	20 0	25-205 25-205
Bartlett	Jour. Am. Chem. Soc., 49, 687, (1927); <i>ibid.</i> , 49, 1955 (1927).	0	50-1000
Bridgman	Proc. Nat. Acad. Sci., 9, 370 (1923); Proc. Amer. Acad. Arts and Sci., 59, 173 (1924).	68	3300-20000
<i>Oxygen</i>			
Amagat	Compt. Rend., 91, 812 (1880).	100	113-418
		14.7	113-418
Amagat	Ann. Chim. Phys., (5), 19, 345 (1880).	20±	32-399
Amagat	Compt. Rend., 107, 522 (1888).	15	1000-3000
Amagat	Ann. Chim. Phys., (6), 29, 68 (1893).	199.5 99.5 15.65 0 15.6 0	150-950 100-1000 100-1000 100-1000 600-3000 100-2900
K. Onnes and Hyndman	Leiden Comm., 78 b; Verslag Akad. Amsterdam, March 1902.	20 15.6 0	23-65 36-51 22-66
Kuypers and K. Onnes	Leiden Comm., 165 a; Archives Néerlandaises, III A, 6, 227 (1923).	20 0	22-61 21-50

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
K. Onnes and Kuypers	Leiden Comm., 169 a; 169 b; Fourth Int. Cong. Refrig. London, June 1924.	-40.05	21-61
		-80.03	21-62
		-102.46	20-60
		-109.97	20-61
		-113.98	20-59
		-116.01	22-55
		-116.99	20-53
van Urk and Nijhoff	Leiden Comm., 169 c; Fourth Int. Cong. Refrig. London, June 1924.	20	36-62
		15.6	34-57
Nijhoff and Keesom	Leiden Comm., 179 b; Verslag Akad. Amsterdam, Oct. 1925, p. 905.	0	37-54
		-40.01	6-9
		-80.00	6-8
		-102.49	5-7
		-109.99	6-7
		-113.94	5-7
		-116.01	5-6
		-116.03	4-5
		-117.01	4-6
		-118.58	4-6
		-124.95	3-6
Holborn and Otto	Zeit. für Physik, 10, 367, (1922).	-135.29	4-6
		-145.39	3-5
		-152.56	3-5
		100	20-100
		50	25-97
		0	25-99
		100 to 0	0-100
Holborn and Otto	Zeit. für Physik, 33, 1, (1925); Wiss. Abh. Phys. Tech. Reich., 9 (1), 163 (1925).	Smoothed	values
Masson and Dolley	Proc. Roy. Soc. London, 103A, 524 (1923).	24.95	30-125
Amagat	Ann. Chim. Phys., (5), 19, 345 (1880).	<i>Air</i>	
		20±	32-400
Amagat	Compt. Rend., 99, 1017, 1153 (1884).	16	26-85
Amagat	Compt. Rend., 107, 522 (1888).	15	750-3000
Amagat	Ann. Chim. Phys., (6), 29, 68 (1893).	200.4	150-1000
		99.4	100-1000
		15.7	100-1000
		0	100-1000
		45.1	800-3000
		15.7	700-3000
Witkowski	Phil. Mag., (5) 41, 288 (1896).	0	100-3000
		100	10-120
		16	10-130
		0	10-130
		-35	50-125
		-78.5	20-130
		-103.5	20-130
		-130	20-80
		-135	30-65

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
		-140	15-40
		-145	15-30
Koch	Ann. der Physik, 27, 311 (1908).	0	26-202
		-79.1	25-200
Holborn and Schultze	Ann. der Physik, 47, 1089 (1915).	200	24-99
		150	21-98
		100	20-98
		50	25-97
		0	25-98
Holborn and Otto	Zeit. für Physik, 10, 367, (1922).	{ 200 to 0 Smoothed	{ 0-100 Values
	Zeit. für Physik, 23, 77, (1924); Wiss. Abh. Phys. Tech. Reich., 8 (I), 41. (1924).		
	Zeit. für Physik, 33, 1 (1925); Wiss. Abh. Phys. Tech. Reich., 9 (I), 163 (1925).		
Penning	Leiden Comm., 166; Archives Néerlandaises, III A, 7, 172 (1923).	20	29-61
		-70.09	52-59
		-84.08	48-58
		-103.48	41-48
		-122.03	34-39
		-129.97	31-36
		-134.99	29-33
		-140.00	27-31
		-145.05	25-28
<i>Carbon Dioxide</i>			
Andrews	Phil. Trans., 159, 575 (1869); ibid., 166, 421 (1876).	6.5	12-34
		13.1	48-90
		21.5	47-63
		31.1	55-85
		32.5	57-85
		35.5	57-108
		48.1	63-109
		63.8	18-223
		100	17-224
Amagat	Ann. Chim. Phys. (5), 19, 345 (1880).	20±	32-400
Amagat	Ann. Chim. Phys., (5), 22, 353 (1881).	100	39-420
		90.2	39-420
		80	39-420
		70	39-420
		60	39-420
		50	39-420
		40.2	39-420
		35.1	39-420
		18.2	105-420
Amagat	Ann. Chim. Phys., (6), 29, 68 (1893).	258	75-450
		198	75-950
		137	50-950
		100	50-1000
		90	50-1000
		80	50-1000

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range, (Atmospheres)
		70	45-1000
		60	45-1000
		50	45-1000
		40	40-1000
		35	40-90
		32	40-78
		30	37-1000
		20	35-1000
		10	33-1000
		0	31-1000
Keesom	Leiden Comm., 88; Verslag Akad. Amsterdam, Sept., p. 391; Oct., p. 533; Nov., p. 616, (1903).	57.75 48.10 41.95 37.09 34.02 31.89 30.98 28.15 25.55	66-136 65-136 65-135 65-136 65-137 64-137 63-139 63-137 63-138
Maas and Mennie	Proc. Roy. Soc. London, 110 A, 198 (1926).	99.9 50.3 19.7 0.1 -24.9 -50.3 -70.2	<1 <1 <1 <1 <1 <1 <1
<i>Methane</i>			
Amagat	Ann. Chim. Phys., (5), 19, 345 (1880).	20 ±	32-400
Amagat	Ann. Chim. Phys., (5), 22, 353 (1881).	100.1 79.8 60.1 40.6 29.5 14.7	53-300 53-300 39-300 39-300 39-300 39-300
Keyes, Smith and Joubert	Jour. Math. and Phys., M.I.T., 1, 191 (1922).	200 150 100 50 0	69-322 61-275 53-228 45-179 36-130
Keyes and Burks	Jour. Am. Chem. Soc., 49, 1403 (1927).	200 150 100 50 0	60-254 53-218 46-182 39-145 32-108
<i>Ethyl Ether</i>			
Ramsay and Young	Zeit. für Phys. Chem., 1, 433 (1887).	280 to 50	1-69
Keyes and Felsing	Jour. Am. Chem. Soc., 41, 589 (1919).	340 to 150	8-41

Author	Reference	Isotherms measured. (Degrees C)	Pressure Range. (Atmospheres)
Beattie	Jour. Am. Chem. Soc., 46, 342 (1924).	325	18-206
		300	17-175
		275	16-143
		250	15-112
		225	14-80
		200	13-48
		175	12-25
		150	11-17

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² Lorentz, Wied. Ann., 12, 127, 660 (1881).

³ Clausius, Wied. Ann., 9, 337 (1880).

⁴ Dieterici, Wied. Ann., 69, 685 (1899); Ann. der Phys., (4), 5, 51 (1901).

⁵ Keyes, Amer. Soc. Refrig. Eng. Jour., 1, 9 (1914); Proc. Nat. Acad. Sci., 3, 323 (1917); Phillips, Jour. Math. and Phys., M.I.T., 1, 1 (1921). The form which this equation takes for an associating gas is discussed by Keyes and Taylor, Jour. Amer. Chem. Soc., 49, 896 (1927); Beattie, *ibid.*, 49, 1123 (1927); Bridgeman, *ibid.*, 49, 1130 (1927).

⁶ (a) The presentation of new experimental pressure-volume-temperature data on gases and the application of the equation to these data are given by Brownlee, Babcock and Keyes, Proc. Third Int. Cong. Refrig., Vol. II, 189 (1913), Chicago [ammonia]; Keyes, Amer. Soc. Refrig. Eng. Jour., 1, 9 (1914) [ammonia and the data of other investigators on eight substances]; Keyes and Felsing, Jour. Amer. Chem. Soc., 41, 589 (1919); *ibid.*, 42, 106 (1920) [ethyl ether]; Keyes, Amer. Soc. Refrig. Eng. Jour., 7, 371 (1921) [ammonia]; Keyes, Smith and Joubert, Jour. of Math. and Phys., M.I.T., 1, 191, 211 (1922) [methane]; Smith and Taylor, Jour. Amer. Chem. Soc., 45, 2107 (1923), *ibid.*, 48, 3122 (1926) [nitrogen]; Beattie, *ibid.*, 46, 342 (1924) [ethyl ether]; Keyes and Burks, *ibid.*, 49, 1403 (1927) [methane].

(b) Some of the applications of this equation to various thermodynamic calculations are presented by Keyes and Kenney, Amer. Soc. Refrig. Eng. Jour., 3, 1 (1917); Keyes, Jour. Amer. Chem. Soc., 42, 54 (1920); *ibid.*, 43, 1452 (1921); *ibid.*, 46, 1584 (1924); *ibid.*, 49, 1393 (1927); Phillips, Proc. Nat. Acad. Sci., 7, 172 (1921); Keyes, Jour. of Math. and Phys., M.I.T., 1, 89 (1922); Keyes, Townsend and Young, *ibid.*, 1, 243 (1922); Smith and Taylor, Jour. Amer. Chem. Soc., 45, 2124 (1923); Keyes and Sears, Proc. Nat. Acad. Sci., 11, 39 (1925); Gillespie, Jour. Amer. Chem. Soc., 48, 28 (1926); Keyes and Marshall, *ibid.*, 49, 156 (1927); Lurie and Gillespie, *ibid.*, 49, 1146 (1927).

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⁸ Amagat, Compt. rend., 94, 847 (1882); Ann. chim. phys., (6) 29, 68, 505 (1893); Ramsay and Young, Zeit. phys. Chem., 1, 433 (1887); Keyes, Amer. Soc. Refrig. Eng. Jour., 1, 9 (1914); Keyes and Felsing, Jour. Amer. Chem. Soc., 41, 589 (1919); Beattie, *ibid.*, 46, 342 (1924); Barus, Phil. Mag., (5), 30, 338 (1890), has shown that the isometrics of liquids are very nearly linear.

⁹ See references under 6 (a).

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¹¹ Keyes and Taylor, Jour. Amer. Chem. Soc., 49, 896 (1927).

¹² See, for instance, Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge (1925), pages 114, 154.

¹³ Clausius, "Die Mechanische Wärmetheorie," Vol. 3, "Die Kinetische Theorie der Gase," F. Vieweg und Sohn, Braunschweig (1891), Chapter II.

¹⁴ Clausius, *Phil. Mag.*, (4), 40, 122 (1870).

¹⁵ Phillips, *Jour. of Math. and Phys.*, M.I.T., 1, 1 (1921).

¹⁶ Clausius, "Die Kinetische Theorie der Gase," loc. cit.

¹⁷ Lorentz, *Wied. Ann.*, 12, 127, 660 (1881).

¹⁸ van der Waals, *Dissertation*, Leiden (1873).—Die Continuität etc., loc. cit.

¹⁹ Boltzmann, "Vorlesungen über Gastheorie," Barth, Leipzig (1896), Part II.

²⁰ Jeans, loc. cit., p. 129.

²¹ van Laar, "Die Zustandsgleichung von Gasen und Flüssigkeiten," Voss, Leipzig, (1924) Chapter 1, §§ 11, 12.

²² Phillips, loc. cit., used the method for the deduction of the volume functions of the Keyes' equation of state.

²³ See Jeans, loc. cit., page 115.

²⁴ Lorentz, loc. cit.

²⁵ Clausius, *Wied. Ann.*, 9, 337 (1880).

²⁶ Boltzmann, loc. cit., Vol. 2, Chapter 6. Cf. also Jeans, loc. cit., p. 193.

²⁷ Gibbs, *Scientific Papers*, Longmans, Green and Co., London (1906), Vol. 1, p. 372.

²⁸ Keyes and Taylor, loc. cit.

²⁹ Boynton and Bramley, *Phys. Rev.*, 20, 46 (1922)

³⁰ Beattie, *Jour. Amer. Chem. Soc.*, 49, 1123 (1927); Bridgeman, *ibid.*, 49, 1130 (1927).

³¹ Phillips, loc. cit.

³² See Bibliography for literature references.

³³ Andrews, *Phil. Trans.*, 166, 421 (1876) converted his measurements on carbon dioxide into both isometric and isopiestic form, and discussed the equation of state from the standpoint of these two methods of treatment of the data.

³⁴ The method used throughout the paper for obtaining the equation of the best straight line through a set of data was to pass a linear equation through the highest and lowest points, and to construct a large scale graph of the deviations from this line. The equation of the best straight line which can be drawn through the deviations was then added to the original equation. The relations given for each isometric in Table IV were obtained in this manner.

³⁵ Keyes, *Proc. Nat. Acad. Sci.*, 3, 323 (1917).

